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THE VELOCITY AND RATIO e/m FOR THE PRIMARY AND SECONDARY RAYS OF RADIUM.

By S. J. Allen.

Introduction.

THE reasons which led the author to investigate this subject ought first to be briefly stated. While trying to demonstrate experimentally the magnetic and electrostatic deviation of the β-rays from radium, by means of the electrical method, I was surprised to find that no appreciable electrostatic deflection could be obtained by the methods at first used, and that moreover the magnetic deflection observed was much less than we would be led to expect from the results of other experimenters. Considering the great importance of this subject, affording as it does the only method we have for testing the behavior of the electron at speeds approaching that of light, it was deemed advisable to make a thorough investigation, and to find out, if possible, wherein lay the difficulties, and the non-success of the early experiments.

Before describing my own experiments it will be of interest to give a brief resumé of the work done by previous investigators on this subject, and the conclusions reached by them. Becquerel[1] was the first to state that the β-rays from radium were deflected in an electrostatic field; and by measuring this deflection, and knowing from earlier experiments the deflection of the same rays in a magnetic field, he was able to calculate their velocity, and the ratio

[1] C. R., 130, 1900.

e/m, e being the charge in electrostatic C.G.S. units, and m the mass expressed in grammes.

His experimental method might be briefly described as follows: A pencil of β-rays was allowed to pass upward between two parallel brass plates, and to fall upon a photographic film, placed horizontally above them. The plates were insulated from one another, and maintained at a high difference of potential by means of an electrostatic machine. A thin sheet of mica was placed vertically in the path of the rays, so as to cut it into two halves. The image on the photographic film would thus be divided into two parts by a fine line in the center. If now on the application of an electrostatic field the rays are bent, then there ought to appear on the image a shadow, the width of which would correspond to the least deviable ray.

Becquerel observed such a shadow, and measuring the width of it, and knowing from other experiments the value of the magnetic deflection, he calculated the velocity of the β-particle to be about 1.6×10^{10} cm. per sec., and the ratio e/m as 1×10^{7}. This experiment of Becquerel was made in air at atmospheric pressure, and for this reason no very accurate estimate of the true electric field between the plates could be made, since the ionization caused by the β-rays would to a great extent disturb the potential gradient. The results of Becquerel can therefore be only considered as approximate.

The method used by Kaufmann[1] to obtain the velocities of the β-rays was entirely different, and was based on the principle of crossed spectra. The heterogeneous pencil of rays from a small speck of radium passed upward between two brass plates, through a small hole in a metal diaphragm, placed horizontally above the plates, and then fell normally upon a photographic plate, wrapped in a thin envelope of aluminium. The brass plates were insulated from one another and could be kept charged to a high difference of potential by means of a battery of small lead accumulators. The whole apparatus was enclosed inside a glass vessel from which the air could be exhausted. A magnetic field was applied parallel to the electrostatic and an exposure given for a certain time; the

[1] Nachr. d. Ges. d. Weis. m. Gott., 1901.

direction of the electrostatic field was then reversed, and a further exposure of the same time as before given, the direction of the magnetic field being the same in both cases. When the plate was developed there appeared on it two curved lines, showing that the β-particles had been deflected by both the magnetic and electrostatic fields. By measuring the deflections observed, the value of the velocity, and e/m for each ray could be calculated. He found that the velocities varied from 2.36×10^{10} to 2.85×10^{10}, and the value of e/m from 1.31×10^{7} to $.63 \times 10^{7}$. Assuming that the charge is constant, these results showed that the mass of the electron apparently increased as the velocity of light was approached.

A theory has been developed by Thomson and elaborated by Heaviside, Abraham and others, whereby the mass of the electron is considered as entirely electrical in its nature, and increases with the speed of the electron, reaching at the velocity of light an infinite value. The late values of e/m obtained by Kaufmann agreed very well with those as calculated from the formulæ of Abraham. I shall discuss these results later on in this paper.

Electrical Experiments.

The electrical method, whenever practical, is in some respects to be preferred to the photographic, in as much as many readings can be made and confirmed in the same time that it takes to make a single exposure by the latter. In my first experiments a sensitive Dolezalek electrometer was used, but it was found almost impossible to shield this and the connecting wires from electrostatic influences sufficiently to obtain accurate readings. It was therefore replaced by a sensitive gold leaf electroscope, which could be shielded very easily from the effects of the high potentials used.

Experiment I. — The first experiment was tried in air at atmospheric pressure, and the general arrangement is shown sketched in Fig. 1. Two zinc plates 18 cm. long were attached to insulating uprights A and B, which kept them in a vertical position about 9 mm. apart. At the bottom of the plates was placed a block of lead containing some radium bromide, covered with a thin sheet of mica, which allowed the β-rays to pass through without much absorption. The radium was so arranged that its extreme edge was in a vertical

line with the plate *b*, thus causing the rays to graze the plate *b*, but allowing them to fall full upon the plate *a*.

Over the top of the plates was suspended the electroscope, the details of which are shown in the figure. The rod *c* carrying the gold leaf was insulated from the case by means of a bead of sulphur *e*. The system was charged to a potential of a few hundred volts by means of the rod *f*, which could be turned so as to touch the rod holding the gold leaf. At other times it was connected to the case, which was earthed. The bottom of the electroscope had a thin aluminum window through which the rays could pass. The time which the gold leaf took to fall through a fixed distance on the cross hair of the telescope was taken as a measure of the ionization. Part of this ionization was due to the β- and secondary rays, and part to the γ-radiations, and these could be distinguished from one another by absorption tests. Of the total about 60 per cent. was due to the γ-, and the remainder to β- and secondary rays.

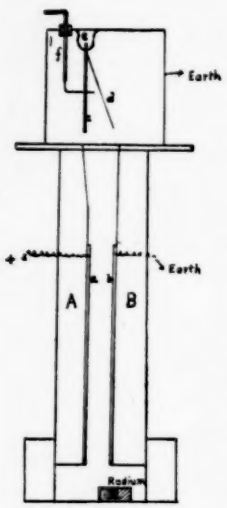

Fig. 1.

If now the plate *a* is charged positively, then the β-rays should be deflected away from the plate *b*, and a decrease of the ionization observed. This decrease would be a measure of the deflection of the rays since no fresh rays could be bent in to take the place of those bent away. If the rays travel at different velocities, then this deflection would be only an average value, but by absorbing the ones of lower velocity one ought to be able to obtain the deflection of the high velocity rays very approximately.

The plates were maintained at a difference of potential by connecting them to a battery of small lead accumulators, from which a maximum potential of 5,000 volts could be obtained. In the later experiments the number of cells was increased, so that a potential difference of about 9,000 volts was available.

When a difference of potential of 5,000 was applied to the plates no appreciable decrease of the ionization in the electroscope could

be observed. The rays were completely deflected by means of a magnetic field, but the value of HR, H being the strength of the magnetic field and r the radius of curvature of the deflected rays, as calculated from this deflection was over five times what it should have been calculated from theory.

The expression for the deflection of the ray in a uniform electrostatic field is :

$$\delta = \frac{Xed\left(\frac{d}{2} + h\right)}{mV^2},$$

where δ represents the deflection, d the distance travelled by the ray in the field, h the distance from the top of the plates to the electroscope, e/m the ratio of charge to mass of the electron, X the strength of the electric field, and V the velocity of the electron. In this experiment $d = 18$ cm., $h = 7$ cm. and $K = 5 \times 10^{11}$ e.m. units.

If we assume for V, and e/m, the extreme values found by Kaufmann, viz., 2.83×10^{10} cm. per sec., and $.63 \times 10^{7}$, the calculated value of the electrostatic deflection for the highest velocity rays amounts to about 11 mm., which should have been observed since the width of the window of the electroscope was only 15 mm.

This failure to observe the electrostatic deflection could not at first be satisfactorily explained, and it was only after a number of experiments by different methods were made that the true explanation was reached. I shall discuss this point later on.

In this experiment, as in all others made in air at atmospheric pressure, we have no very definite knowledge of the uniformity of the electric field between the plates, and for this reason all the remaining experiments were carried out in a vacuum. In this case the plates can be placed closer together, and a much higher potential applied between the m without a discharge taking place, the field between the plates being practically uniform.

Experiment II. — In Fig. 2 is sketched the general arrangement of this experiment. Two zinc plates, a and b, 6 cm. long are insulated from one another, and kept a distance apart of 2.9 mm. by means of ebonite side pieces. Beneath the plates are fastened two ebonite blocks, forming between them a slit of about 1 mm. width,

through which pass the rays from the radium contained in a capsule placed below. The capsule is covered with a thin sheet of mica, and sealed so that no emanation from the radium can escape into the surrounding vessel.

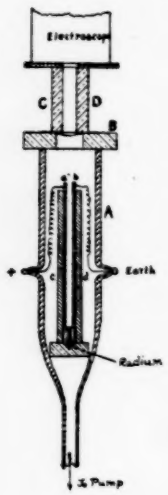

Fig. 2.

This apparatus was then enclosed in a glass vessel *A* from which the air could be exhausted to a high vacuum. The top of the vessel was closed by means of a brass cap *B*, which had an opening cut through it, and covered with a very thin sheet of zinc. Two wires sealed through the glass were connected to the two plates, and served to charge them to any desired potential difference.

On top of the brass cap were placed two parallel brass blocks, 3 cm. long and at a distance apart of 1 cm., which supported the electroscope.

The rays from the radium passed upward in a diverging beam, through the thin sheet of zinc, and into the electroscope. When the vessel was exhausted to a high vacuum the plates maintained a potential difference of 5,000 volts without a discharge; in this case we can assume that the electric field between the plates is uniform. When this voltage, which corresponds to an electric field of about reach the electroscope will consist in a large part of those of medium 10–15 per cent. in the ionization due to β-rays. The rays which 17,000 volts per cm., was applied there was a decrease of about and high velocities, since the low velocity rays are mostly absorbed in the zinc plate. If we calculate as before the deflection which might be looked for we find it to be about 8.2 mm. for the highest velocity rays, and since the distance between the plates at the electroscope is only 10 mm. this would amount to over 80 per cent. complete deflection. Those rays of lower velocity would be completely deflected. When the apparatus was placed in a magnetic field the rays could be completely deflected, though the apparent value of HR obtained was over three times what might be looked for.

There was a slight possibility that some of the emanation might have escaped into the vessel, in which case the true effect would be

to some extent masked by the rays coming from the emanation. In order to prevent this possibility another arrangement was devised where the radium was kept entirely outside the vessel containing the charged plates.

Experiment III.— The experimental arrangement is shown in Fig. 3. A series of zinc plates, *a*, *a*, *a*, etc., 18 in number, were arranged parallel to one another, being insulated and kept apart by means of ebonite side strips. This arrangement was enclosed inside a glass vessel *A*, which had the walls blown out in thin bulbs immediately above and below the system of parallel plates. Alternate plates were connected together and to one electrode, the remaining plates being joined to the other electrode. The length of the plates was 4 cm., and the distance apart 1 mm. The radium was placed beneath the plates, and the electroscope above. By this arrangement a much greater amount of β-rays could get into the electroscope than in the previous experiments, and also a large electric field could be produced between the plates. A small deflection of the rays should be readily detected in the electroscope. The radium was placed about 4 cm. from the bottom of the plates, so that the increase due to rays being bent so as to enter the electroscope could not be great enough to offset the decrease due to rays bent away and absorbed.

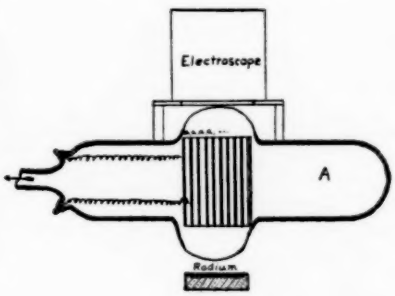

Fig. 3.

When a difference of potential of 5,000 volts was applied to the plates no very appreciable deflection could be observed. The magnetic deflection was also considerably less than one might expect from theory. The total thickness of the glass walls would have about the same absorbing power as the sheet of zinc in the previous experiment.

The results of these experiments were at first very perplexing, and no very satisfactory explanation could be reached. One was loath to conclude that the β-rays were not deviable in an electrostatic

field, since Kaufmann in his carefully carried out experiments obtained results which were in such extremely good agreement with theory. Besides, the disagreement of the magnetic results with those obtained by other experimenters, seemed to show that there were present some phenomena which were affecting both alike. Nothing has been said thus far in these experiments concerning the effect of the secondary rays which are produced when the β- and γ-rays strike upon various substances. This effect was from the first considered, and was thought to be too small to account for the results obtained, but, after some further experiments, the conclusion was reached that it played in all the experiments a large rôle and in some cases the principal one.

When the β-rays, cut down to a narrow pencil by means of slits, were allowed to pass through an opening in the bottom of the electroscope considerably wider than the supposed width of the pencil, it was found, on placing a narrow strip of lead over the opening in different positions to cut off only a portion of the opening at one time, that the decrease in ionization was the same for any part of the opening. This showed clearly that the rays coming through the opening were not confined to a narrow pencil, as supposed, but spread out into a diffuse, uniformly distributed beam.

A photographic plate placed over the opening showed on development a broad, uniformly dense image, instead of the sharp narrow one, which ought to be made by the β-rays alone. This broadening of the pencil of the rays is unquestionably caused by the secondary radiation produced by the primary β- and γ-rays. If this secondary radiation was of the nature of γ-rays, then it would not be deflectable in a magnetic or electrostatic field, and could consequently not affect the deflection of the β-rays, but if, on the other hand, it was of the nature of the primary β-rays, and therefore deflectable, great confusion would arise from the different radiations.

The secondary radiation produced by β- and γ-rays of radium has been the subject of investigation by McClelland,[1] Eve[2] and Kucera,[3] who found that in general it is of several kinds, both deflectable and

[1] Phil. Mag., February, 1905.
[2] Phil. Mag., December, 1904.
[3] Annalen der Physik, 1906.

non-deflectable in a magnetic field, and of different penetrating power. No definite knowledge was obtained of the velocities of the deflectable kind, and to this purpose the author decided to make a complete investigation of the secondary rays. Before giving an account of this investigation I would like to describe two experiments on the β-rays made by the photographic method.

Photographic Experiments.

Experiment I. — The arrangement used in this is essentially the same as that used by Becquerel[1] and is shown sketched in Fig. 4. Two metal plates *a* and *b* 4.2 cm. in length were placed parallel to one another in a vertical position 6 mm. apart, and insulated by means of ebonite. About 2 cm. below the plates was placed the radium, contained in a narrow crevasse in a block of lead. In the center of the radium, and midway between the plates was fastened a sheet of mica *c*, which extended from the radium up to the photographic plate *e*. This plate was wrapped in a sheet of black paper, and then placed inside a light tight box containing a thin aluminium window, through which the rays could pass without much absorption. The distance between the top of the metal plates and the photographic plate was 2.4 cm.

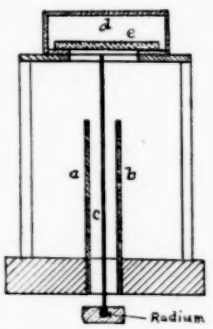

Fig. 4.

When the plates *a* and *b* are uncharged there ought to be obtained on the photographic plate an image crossed in the center by a narrow band. On the other hand when the plates are charged to a high potential if the rays are deflected to one side, the photographic plate should show a broad shadow cast by the mica screen. In *A* and *B*, Fig. 5, are shown two photographs obtained by this method, *A* taken without an electric field, and *B* with a potential difference between the plates of 3,000 volts, corresponding to a field strength of 6,000 volts per cm. Both photographs appear precisely alike and show no indication of any shadow on the plate. One side in both photographs appears darker than the other; this

[1] Loc. cit.

is on account of the mica screen not being placed exactly in the middle of the radium, thus throwing more rays to one side than to the other. In *C* and *D* are shown two photographs taken with the screen placed exactly in the center, *C* being without a field and *D* with one ; and both sides of the image now appear equally dense. These photographs were all taken with the radium covered with a thin sheet of mica, so that no emanation could escape and affect the plate. Experiments were also tried with the radium uncovered, and the same results were obtained as before. Radium when dry and at ordinary temperatures does not give off very much emanation.

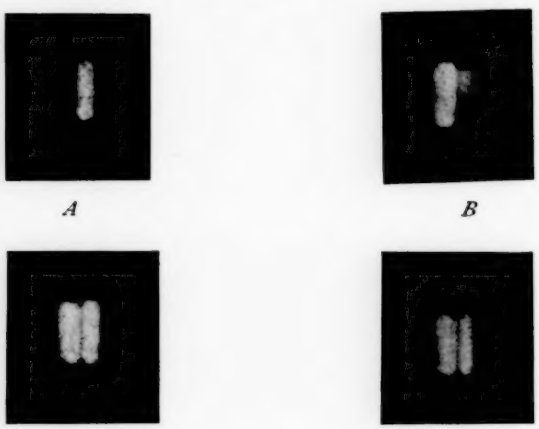

Fig. 5.

Experiment II. — The arrangement used in this experiment, and illustrated in Fig. 6, is essentially the same as that used by Kaufmann [1] in his work. Two brass plates, *a* and *b*, placed parallel to one another inside a brass box *A*, were insulated from the sides by means of ebonite bushings *c* and *d*. Beneath the plates was fastened a small speck of radium bromide, and above the plates a thick ebonite screen, which had a hole 0.5 mm. cut in it through which the rays could pass in a narrow pencil. At the top of the brass box was placed a photographic plate wrapped in a sheet of black paper. The whole apparatus was enclosed inside a glass vessel which could be exhausted to a high vacuum.

[1] Loc. cit.

Exposures of one, two and four days were made, with and without an electric field, but in no case could any sharp image due to β-rays be obtained on the plate, the only effect being a darkening of the whole plate due to γ- and secondary radiations. When the radium was left uncovered the darkening of the whole plate was much greater, due to the emanation diffused throughout the vessel.

In another arrangement a larger quantity of radium contained in a lead capsule was placed outside the brass box, and the rays allowed to enter through a small hole, and thence through an ebonite diaphragm placed just beneath the brass plates *a* and *b*.

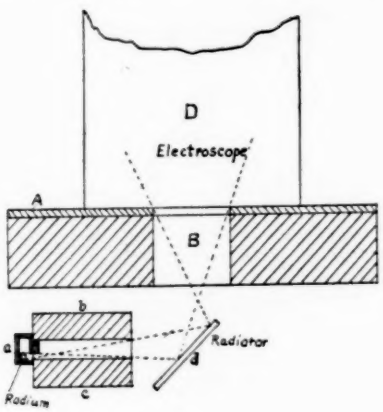

Fig. 6.

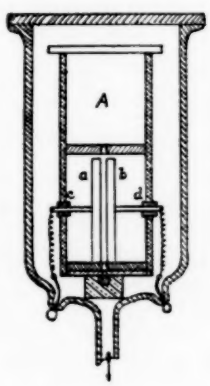

Fig. 7.

This failed to give any better results than before; and all further attempts to repeat Kaufmann's experiment were then abandoned. Probably with better photographic skill in restraining the darkening effect due to γ- and secondary rays I might have succeeded in obtaining a clear image of the β-rays. The radium used in this experiment was some kindly loaned me as that used by Kaufmann in his last experiments, if not stronger.

Secondary Radiation.

The experimental arrangement used to study the secondary radiation is shown diagramatically in Fig. 7. About 300 milligrammes of radium bromide of about 30,000 activity was sealed in a very thin glass tube of 1.5 mm. diameter and about 5 cm. long. This tube was

enclosed inside a lead box *a*, which had a slit 5 cm. long and 1 mm. wide cut in one side, the walls of the lead box being of such a thickness that no β-rays could pass through. This box was cemented to two thick ebonite blocks *b* and *c* in such a manner, that one edge of the slit coincided with a face of one of the blocks as indicated in the figure. A divergent beam of β-rays thus emerged from the slit and was limited in width by the walls of the ebonite blocks. This apparatus was placed so that the rays traveled in a horizontal direction.

Directly above and parallel to the ebonite blocks was supported a thick screen *A*, constructed of cardboard and filled with mercury, and having in the center a wide rectangular opening through which the radiations could pass into a gold-leaf electroscope placed above. The substances which were to be studied as sources of secondary radiation were placed beneath this opening in such a position that the β-rays fell full upon them. The thick mercury screen absorbed a large part of the γ-radiation; and although it introduced a small amount of secondary radiation, this increase was more than offset by the decrease of the γ-rays. The ionization in the electroscope, due to the secondary radiation from below, would under these conditions form a much larger proportion of the whole than when the full γ-rays were present.

When the radiator *d* is not present, the ionization in the electroscope is due to γ-rays and to secondary rays produced by them.

When the radiator is placed in position this ionization will be increased by that due to the secondary rays from below. By fixing radiators of different materials in the position *d*, and placing screens of varying absorbing power under the opening *b*, a knowledge of the relative penetrating power of the secondary radiations from the different radiators can be obtained. When a thick screen is placed so as to cut off the β-rays, then the increase of ionization will be due to the secondary rays caused by the γ-rays striking the radiator *d*.

In Table I. are shown a characteristic series of readings for different radiators, under various conditions.

TABLE I.

Radiator—Air and Surrounding Objects.

Total Rate of Leak.	Rate of Leak Due to Secondary Rays.	Absorbing Material.	Per Cent. Unabsorbed Rays.	Remarks.
3.61	1.01	0	100	No radiator at *d*.
3.02	.42	4 sheets paper	41	Paper placed on top of
2.94	.34	8 " "	34	mercury screen.
2.85	.25	16 " "	25	
2.70	.10	34 " "	10	
3.28	.68	50 " "		Paper placed below screen
3.29	.69			placed over β-rays.
		Radiator—Zinc.		
10.20	7.10	0 paper	100	In this set of readings the
8.85	5.75	2 "	81	absorbing layers of paper
7.76	4.66	4 "	66	were placed directly over
6.21	3.11	8 "	44	radiator *d*.
4.74	1.64	16 "	23	
4.09	.99	24 "	14	
3.53	.43	40 "	6	
3.28	.18	60 "	2.5	
		Radiator—Zinc.		
5.00	1.90	0 paper	100	β-rays partly screened by
4.51	1.41	4 "	74	24 sheets of paper.
4.18	1.08	8 "	57	
3.80	.70	16 "	37	
3.82	.72	0 "	100	β-rays screened by piece
3.59	.49	20 "	68	of zinc.
3.42	.32	36 "	44	
3.31	.21	86 "	29	

Total Rate of Leak.	Corrected Leak.	Absorbing Material.	Per Cent. Unabsorbed Rays.	Remarks.
3.82	.72	0	100	Zinc screen over β-rays.
3.30	.20	0	100	2 zinc screens over β-rays.
3.24	.14	100	70	2 zinc screens over β-rays.
Air, 3.10	.00	0	0	Radiator removed.
		Radiator—4 Sheets of Paper.		
4.96	1.86	0	100	
4.18	1.08	4	58	
3.69	.59	8	31	
3.34	.24	10	13	
3.21	.11	32	6	

Radiator—8 Sheets of Paper.

5.29	2.19	0	100

Radiator—16 Sheets of Paper.

5.81	2.71	0	100

Radiator—28 Sheets of Paper.

6.45	3.35	0	100
4.80	1.70	4	51
4.13	1.03	8	31
3.57	.47	16	14
3.29	.19	32	6
3.23	.13	82	4

Radiator—Glass.

7.52	4.42	0	100
4.86	1.76	8	39

Radiator—Lead.

11.36	8.26	0	100
6.85	3.75	8	45

Radiator—Copper.

Total Rate of Leak.	Corrected Leak.	Absorbing Material.	Per Cent. Unabsorbed Rays.
8.88	5.68	0	100

Radiator—Iron.

8.69	5.59	0	100
5.34	2.24	8	40

From a study of these results we see at once that substances when struck by β-rays give out secondary rays which differ amongst themselves both in quantity and penetrating power.

In order to produce the maximum amount of secondary rays the substance has to be of sufficient thickness to completely absorb all the β-rays which fall upon it. The amount of secondary radiation due to the γ-rays is only a very small quantity of the total, provided the thickness of the radiator is only just sufficient to absorb all the β-rays. When only the most penetrating β-rays are allowed to fall upon the radiator, the secondary radiations produced are on an average of a much more penetrating nature, than when all the β-rays are present. This is partly due to the fact that the secondary rays due

to the high velocity β-rays are more penetrating, and also partly to the presence of a small amount of secondary γ-rays caused by the primary rays. The denser a substance is, the greater will be the amount of the secondary rays produced, and the greater their penetrating power. Of those substances examined, lead proved to be the most efficient, and also gave rays of the most penetrating power, while paper was the least. For the sake of comparison I give in Table II. the results of an absorption test on the primary β-rays (which of course contained a certain amount of secondary rays), together with the results obtained for the secondary radiation from zinc and paper.

TABLE II.

Layers of Paper.	Primary β-Rays.	Secondary from Zinc.	Secondary from Paper.
0	100	100	100
2	82	81	
4	70	66	51
8	52	44	31
16	33	23	14
24	22	14	
32	15		6
44	9.7	5.8	
60	5.0	2.5	

The penetrating power of the secondary rays from zinc does not differ very greatly from that of the primary β-rays, especially for the first few sheets of paper. The penetrating power of the sec-

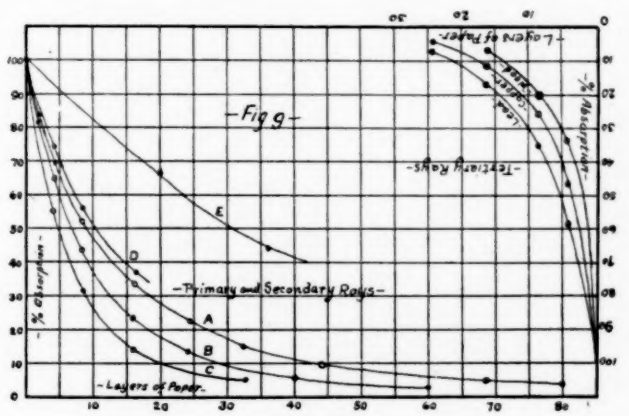

Fig. 8.

ondary rays from lead is only slightly greater than that of the rays from zinc.

In Fig. 8 are drawn several absorption curves, both for the primary β-rays, and for the secondary rays. A represents that for the primary β-rays, B that for the secondary rays from zinc, C that for the secondary from paper, D the secondary from zinc when the primary β-rays have passed through 28 sheets of paper, and E that for the secondary from zinc when the primary β-rays have passed through one sheet of zinc. It is seen at once from these curves that the radiations are not homogeneous, but travel at different velocities.

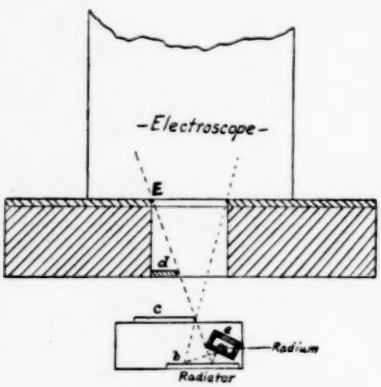

Fig. 9.

It is well known that a part of the secondary rays are deviable in a magnetic field, and in the same direction as the β-rays would be. The magnetic deflections of the secondary rays from lead, and from paper, were tried by the method illustrated in Fig. 9. The primary β-rays from the radium enclosed in the lead box a striking the radiator b, produced secondary rays which passed up into the electroscope. Screens of lead c and d were so placed that the secondary rays from the radiator could just touch the upper edge E of the mercury screen. Experiments were performed with both lead and paper as radiators, and in both cases it was found that the secondary

TABLE III.

Field Strength.	Per Cent. Undeflected Rays.	
	Lead.	Paper.
0	100	100
90	66	58
180	36	34
270	21	28
380	11	14
450	8	10

rays produced were deflected towards the right, when a magnetic field was applied in such a direction, that the lines of force can be represented as going into the plane of the paper. The results obtained in this experiment are expressed in the preceding (Table III.).

These results show that the secondary radiations from both metals and insulators consist for the most part of negatively charged particles. Those from insulators are more easily deflected than those from the more dense metals, but the difference is not very great. The proportion of non-deviable rays in the secondary rays from paper is greater than in that from zinc.

Tertiary Rays.

When the secondary radiation strikes upon objects there is produced a third type of radiation called the tertiary rays. This radiation has been studied in the present investigation for a few substances. The method employed was precisely the same as that used for the secondary rays, with the exception that the small glass tube containing the radium, instead of being placed in front of the opening in the lead box, was moved to one side, so that no β-rays could emerge from the opening. Under these conditions the β-rays will strike the lead walls of the lead box and produce secondary rays which will travel out through the opening.

If we place a radiator in the same position as before, there will be produced in it tertiary rays, which can pass up to the electroscope, and cause an increase of ionization. The penetrating power of these rays was studied lor lead, zinc and copper radiators, and the results are expressed in the following table.

Table IV.

Layers of Paper.	Tertiary Radiations.		
	Lead.	Zinc.	Copper.
0	100	100	100
4	59	46	47
8	35	25	24
16	17	10	11
24	6		2.4

As in the case of the secondary rays, lead proves to be the most efficient radiator, and also gives out the greatest penetrating rays. The penetrating power of the tertiary rays is considerably less than that of the secondary, that for lead in the former being only slightly greater than that for paper in the latter.

To find out whether the tertiary rays were deviable in a magnetic field, the arrangement shown diagrammatically in Fig. 10, was made use of. The mercury screen A was placed so that one end was directly over the ends of the ebonite blocks a and b. The electroscope B was placed near to the edge of the screen A, and had a window c covered with thin foil cut in one side, so that any rays might enter without absorption.

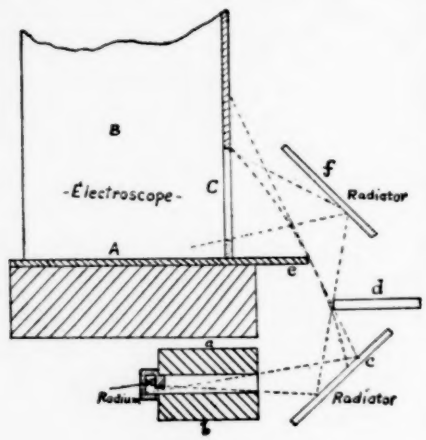

Fig. 10.

When the screen c was placed in position the tertiary rays produced could travel upward and enter the electroscope. Now by placing two screens, d and e, in the positions indicated in the figure, the rays could be prevented from entering the electroscope, but a portion would still be able to travel upward. When a magnetic field was applied in such a direction that the lines of force were perpendicular, and going into the plane of the paper, the ionization in the electroscope was not appreciably altered, but when applied in the reverse direction there was observed an increase in ionization. Moreover, when a screen was placed so as to cut off entirely the tertiary radiation from below, this effect was still observed but to a much less degree. These two results indicated that there was present, besides the tertiary radiation from below, a radiation which seemed to come from the mercury near the window of the electroscope. This latter radiation is undoubtedly caused by the γ-rays when they emerge from the surface of the mercury, and is the same as that observed by Eve[1] when the γ-rays were partly absorbed

[1] Loc. cit.

by a thick block of lead. By placing sheets of paper in front of the window, it was found that the penetrating power of this radiation was much less than that of the tertiary; 4 sheets of paper cut it down to 30 per cent., and 16 sheets completely absorbed it. It was also observed that when the magnetic field was increased slowly from zero, a certain strength was reached at which the increase of ionization in the electroscope due to the tertiary rays from below just became noticeable. When this happened, the rays from below were bent so that the extreme edge of the beam just entered the window. Knowing three points on the circular path of the rays the radius of curvature could at once be calculated, and was found to be about 17 cm. The strength of the magnet field was about 90 C.G.S. lines, so that we get for the tertiary rays a value of $HR = 1{,}530$ approximately. These results show that the tertiary rays are deviable in a magnetic field in the same direction as the β- and secondary radiation. They must therefore be negatively charged particles travelling at speeds only a little less than the slowest β-particles.

When the screen f is placed in the position indicated in the figure, it was found that the ionization in the electroscope was increased. This was found to be partly due to the secondary rays produced when the rays strike the screen, and also partly caused by the tertiary rays from below striking the screen, and producing a fourth type of rays.

That this latter radiation is present, can at once be shown by placing in front of the blocks a and b a screen, sufficient to cut off all the secondary rays, in which case the fourth rays are absent. This process would probably go on for a large number of radiators, but after the third the radiation is too feeble to be measured accurately. Each type of radiation is of less penetrating power than the one which produced it.

Velocity and Ratio e/m for the Primary β-Rays.

It has just been shown that the secondary β-rays have nearly the same penetrating power as the primary, and therefore, assuming for the present that they possess the same charge and mass, they must travel at velocities only slightly less. After passing through a cer-

tain thickness of absorbing material, the lower limit for both types of rays would be the same, and consequently the forward edge of a deflected beam would consist of both primary and secondary rays of the same velocity, which were just able to pass through the absorbing layer and cause ionization.

As the thickness of the absorbing layer is increased the less penetrating radiation would be more quickly absorbed, and at very thick layers, the edge of the deflected beam would consist almost entirely of the more penetrating radiation.

If, then, by any method we can find the forward edge of the deflected beam in both magnetic and electrostatic fields, we can at once calculate the velocity of those rays, both primary and secondary, which are just able to cause ionization after passing through the absorbing layer. The following method was then devised for this purpose and proved successful. It is shown illustrated in Fig. 11.

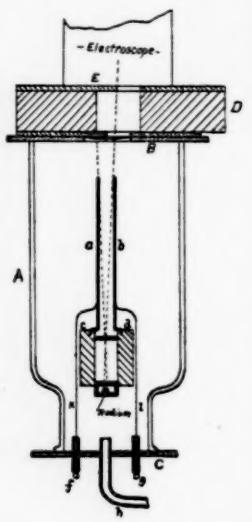

Fig. 11.

Two zinc plates, *a* and *b*, were supported in a vertical direction, and insulated from one another by means of the ebonite blocks, *c* and *d*. At the bottom of these blocks was fastened the lead box containing the glass tube of radium, and furnished with a slit 1 mm. in width, through which the rays emerged. At a short distance below the zinc plates there was placed a lead diaphragm with another slit also 1 mm. in width, which formed with the opening below a narrow pencil of rays, which travelled upward between the zinc plates. The distance between the two slits was such that the rays from the radium just touched the top edges of the plates. This apparatus was placed inside a glass vessel *A*, which was closed at the top and bottom with brass plates *B* and *C*. Through the top plate *B* there was cut a rectangular opening 1.5 cm. in width, and then covered with as thin a sheet of mica as would stand the pressure when the vessel was exhausted. The thickness of this mica window was about equivalent in absorbing power to six sheets

of ordinary writing paper. The bottom plate C was pierced with three holes, into which glass tubes were fitted, two of them, f and g, containing the connecting wires, K and L, and the third, H, serving to connect the vessel to the pump.

The whole apparatus was rendered air-tight by the aid of sealing-wax; and it was found that, with an occasional stroke of the pump, the pressure could be maintained low enough to withstand a potential difference of 10,000 volts without a discharge taking place.

By connecting the wires, K and L, to the poles of the battery of lead accumulators, the zinc plates could be charged up to any desired difference of potential. In the meantime the number of the cells had been increased so that a maximum potential of 9,000 volts could be obtained.

On top of the brass plate B was placed the mercury screen D, described in the previous pages, which served to cut down in a large measure the γ-rays. The opening in this screen was partly covered at the top by a brass plate E, so placed that no β-primary rays could enter the electroscope. The ionization in the electroscope would then be caused by γ- and secondary rays.

The vessel was placed between the poles of a large electromagnet, of such a size that the rays during their entire course lay in a uniform field.

When the primary rays strike the sides of the slits in the lead diaphragms, secondary rays are produced which travel upward with the primary to the electroscope. The pencil of rays at the electroscope is then made up of both primary and secondary radiation, but will be prevented from entering by the brass screen E. This pencil of rays will, however, be confused by the presence of other secondary and tertiary rays coming from various points. This could be illustrated by some photographs taken at different points along the path of the rays. One taken 1 cm. from the upper slit shows a narrow fuzzy image, whereas at 1 mm. from the top of the zinc plates the image is sharp and the full width of the opening. At the top of the plate B the image had again become indistinct, while at the top of the mercury screen it was of the full width of the opening and of uniform density.

If the opening at the electroscope was arranged symmetrically

with regard to the zinc plates, there was observed a decrease of ionization in the electroscope when the magnetic or electrostatic fields were applied in either direction. The decrease in the case of the electrostatic field was about 25 per cent., with a strength of field of 14,000 volts per centimeter. This shows clearly that the rays are deflectable in an electric field, though the effect observed was only about one quarter as much as might be expected.

When, however, the arrangement was the same as that described in Fig. 11, altogether different results were obtained. If the plate *a* were charged negatively, the ionization increased gradually to a maximum with increase of field, remained constant for a period, and then decreased. If, on the other hand, the plate *a* is positive the ionization decreased at once. The reason for this can be explained in the following manner.

If the plate *a* is charged negatively, the primary and secondary β-rays will be deflected to the right, and enter the electroscope, thus causing an increase of ionization.

This increase will continue until the rays have just reached the opposite side of the opening into the electroscope. When this is the case we can assume that those rays which after passing through the absorbing layer can just affect ionization, are bent the most, since all rays of lower velocity, and hence penetrating power, cannot get through the layer. The same phenomena exactly were observed when a magnetic field was applied. Consequently when the maximum point is reached for both magnetic and electrostatic deflection, the value of the velocity of the slowest ray, which can just get through the absorbing layer, can at once be calculated from the values of the electrostatic and magnetic fields. When different thicknesses of absorbing layers were placed over the opening, the strength of fields necessary to produce the maximum ionization was found to increase with increasing thickness of layer. This is what we would expect if the rays are of all different velocities, and shows, that when the maximum point is reached, the least penetrating rays for each successive layer have all been bent through the same distance.

For the sake of illustration some of these results are expressed in the accompanying table (V.).

TABLE V.

Through 6 Sheets Paper.		14 Sheets Paper.		1.5 mm. Glass.	
P. D.	Rate of Leak.	P. D.	Rate of Leak.	P. D.	Rate of Leak.
0	144.0 sec.	0	151.0 sec.	0	154.0 sec.
2,700	134.4 "	3,400	144.2 "	4,000	151.0 "
3,000	132.4 "	3,600	143.4 "	5,600	149.4 "
3,300	131.6 "	3,900	142.8 "	5,800	148.6 "
3,400	131.2 "	4,100	141.5 "	6,000	148.4 "
3,560	131.0 "	4,300	141.5 "	6,800	148.6 "
3,800	130.8 "	6,000	141.4 "		
5,000	130.6 "				
6,000	130.6 "				
Max. 3,500 volts.		4,100 volts.		6,000 volts.	

In this method we do not know how far each ray is bent, since we do not know its first position, and therefore cannot obtain values of mv/ε, and mv^2/e, but, since the deflection is small compared to the length of the path, we can assume without any great error, that, for a maximum, this is the same for both magnetic and electric deflection. By comparing the electric and magnetic forces on the particle we can at once estimate its velocity. If d is the distance travelled by the ray in the uniform magnetic field H, l the length of the zinc plates, h the distance from top of plates to electroscope, X the strength of electric field, the velocity V is given by

$$V = \frac{2Xl\left(\frac{l}{2} + h\right)}{Hd^2}.$$

In this experiment, $d = 17.0$ cm., $l = 8.4$ cm., $h = 5.5$ cm., and the distance apart of the charged plates was 6.2 mm., therefore,

$$V = \frac{2X \times 8.4\left(\frac{8.4}{2} + 5.5\right)}{17 \times 17 \times H} = \frac{0.563X}{H}.$$

As an example take the results for an absorbing layer of six sheets of paper; here $X = 3{,}500/0.62 = 5.7 \times 10^{11}$ C.G.S. units and $H = 13.5$ C.G.S. lines, and therefore we obtain,

$$V = \frac{0.563 \times 5.7 \times 10^{11}}{13.5} = 2.37 \times 10^{10} \text{ cm./sec.}$$

In order to obtain values for e/m, it is necessary to know either mV/e, or mV^2/e, for the different rays. Values of mV/e were obtained by the following method.

The lead-box containing the radium tube was fastened to the ebonite blocks as before, but the distance between these narrowed to 2 mm., and the upper lead diaphragm removed. This arrangement allowed a broader pencil of rays than in the previous experiment to pass upward to the electroscope. Two zinc plates 3 cm. in height were fastened to the ebonite blocks in a vertical direction and so arranged that one edge of the pencil of rays could just touch the top of one of the plates. The effect of this upper plate was then to define sharply a pencil of both primary and secondary rays. This arrangement was then surrounded by a magnetic screen of soft sheet iron, which extended up to the top of the zinc plates, and kept the rays during their passage between the plates from the action of the magnetic field. The glass vessel was dispensed with and the experiment performed at atmospheric pressure, sheets of paper equivalent in absorptive power to the mica window of the previous experiment being interposed in the path of the rays. The opening at the electroscope, 1 cm. in width, was arranged as in the other experiment so that no rays of this pencil could enter the electroscope.

When a magnetic field was applied in the proper direction the ionization in the electroscope gradually increased to a maximum as the strength of the field was increased. Since the rays are only under the action of the magnetic field during their passage from the top of the zinc plates to the electroscope we can assume that, when the maximum point is reached, the least penetrating rays have been deflected over the distance represented by the width of the opening. By placing in the path of the rays suitable thicknesses of absorbing material the value of mV/e for the same rays as were observed in the previous experiment could be ascertained.

These values were calculated from the following formula:[1]

$$\frac{mV}{e} = \frac{1}{2\delta}\int dx \cdot \int H dx,$$

where δ is the distance through which the rays are bent, and H the

[1] See J. J. Thomson's Discharge of Electricity through Gases, page 92.

value of the magnetic field at different points along the path x of the rays. The value of mV/e obtained by this method was 1.57×10^3 for no absorber, whereas, for 1.2 mm. of zinc it was 5×10^3; for 6 sheets of paper corresponding to the mica window the value was 1.87×10^3.

In the former experiment in the uniform field the value of

$$\frac{mV}{e} = \frac{Hd^2}{2\delta},$$

and substituting the value of mV/e obtained above, we get for the distance through which the rays were bent 1.04 cm. Knowing this value of δ, all the remaining values can at once be calculated, and the complete results are shown in the following table (VI.).

TABLE VI.

Absorbing Layer.	$X_{(max.)}$	$H_{(max.)}$	mV^2/e	mV/e	V cm./sec.	e/m
0				1.57×10^3	2.20 (est.)	1.40
6 of paper.	5.7×10^{11}	13.5	4.4×10^{13}	1.87	2.37×10^{10}	1.27×10^7
10 "	6.1	14.3	4.76	1.98	2.40	1.21
14 "	6.6	15.1	5.15	2.10	2.45	1.17
18 "	7.2	16.2	5.62	2.25	2.49	1.10
22 "	7.7	17.0	6.01	2.36	2.54	1.07
30 "	8.3	17.9	6.47	2.49	2.60	1.04
1.5 mm. glass.	9.6	20.0	7.49	2.78	2.69	.96
.3 copper.	11.0	22.2	8.58	3.09	2.77	.90
0.4 zinc.	14.0	27.2	10.92	3.79	2.88	.76
.8 "				4.60	2.95 (est.)	.64 [1]
1.2 "				5.00	2.97	.59 [1]

As has already been explained, the values given in the above table will represent those for both the primary and secondary particles which are just able to penetrate through a certain absorbing layer and still cause ionization; the highest values of the velocity are those for the β-particles alone, since nearly all the secondary particles are absorbed in about 35 sheets of paper. The values of the velocity for the particles through 0.8 and 1.2 mm. of zinc could not be obtained for the reason that the limit of the available difference of potential had been reached. The values of mV/e for these, however,

[1] These estimated values were extrapolated from the curve showing the relation between the velocity and mV/e.

show that the apparent mass of the particles is increasing rapidly as the velocity of light is approached. The lower limit of the β-rays cannot be stated with any certainty, but it is probably greater than 2.3×10^{10} cm. per sec. The β-rays in all the experiments had first of all to pass through the thin glass walls of the tube, which would probably absorb about as much as the mica window.

The results given in the above table agree very well with those obtained by Kaufmann [1] in his later experiments, using an entirely different method, and show beyond doubt that the β-particles from radium travel with speeds approaching that of light, and further that their apparent mass does increase with the speed.

In Kaufmann's experiment secondary radiations must have been present in quantities quite comparable with the primary, and consequently any point chosen on his curved photographic traces would represent not alone the primary particle, but also some secondary particles which happened to arrive at the same point. If the primary and secondary particles differed in velocity there might possibly be some difficulty in estimating the radii of curvature for the different rays. He has compared his results with those calculated from the theoretical formulæ of Abraham, and finds a very close agreement, thus giving considerable evidence to the view that the mass of the electron is entirely electrical in origin, and increases as the speed approaches that of light. The result of the present investigation also seems to lead to the same conclusion. We must, however, remember that the confirmation of this theory is only over a short range where the increase of the apparent mass is is not very great, and where any set of values might accidently agree very closely with the theoretical. It is not until the speed has, for all experimental purposes, practically reached that of light that there is any great increase of the apparent mass, and consequently any confirmation of the theory over a long range is entirely beyond experimental means. Moreover, the assumptions made in the derivation of the theoretical fomulæ, and also in the formulæ used to calculate the velocities and ratio e/m from the experimental data, are many and somewhat great. It is assumed that the same laws of electric and magnetic force apply equally well, at very high

[1] Loc. cit.

speeds, as at comparatively low, something of which we have no *à priori* knowledge. A divergence of either, or both, of these laws at high speeds could account for the experimental facts observed.

However considering all sources of error, the results of Kaufmann, together with those of the author, lend great weight to the view that the mass of the electron is electrical in origin, and increases with the speed.

Velocity and Ratio e/m for the Secondary β-Rays.

It has been assumed in the previous sections that the velocity of the secondary rays was only slightly less than the primary, and also that they carried the same charge and had approximately equal masses. That these facts are true was proved by the following set of experiments.

The general arrangment of the experiments was the same as that used in the case of the primary rays, and the same drawings and general description will suffice here. The tube of radium, instead of being placed underneath the slit in the lead box, was shifted to one side so that no primary rays could emerge from the box. The lead box was fastened to the ebonite blocks so that the slit was near the right-hand block, and not in the middle as was the case with the primary rays. The upper lead diaphragm was removed and in its stead was fixed a strip of lead, which covered one third of the opening between the blocks. The secondary rays on emerging from the slit in the lead box could strike full upon the left-hand zinc plate, but were prevented by this strip of lead from falling upon the right-hand plate. The rest of the arrangement was precisely the same as for the primary rays, the opening at the electroscope being arranged so that no secondary rays from the lead box could enter.

The secondary rays when they strike the left-hand plate, and also the edge of the lead strip, produce tertiary rays which travel up with the secondary rays. A great part of these will be absorbed by the mica window but some will get through and cause ionization in the electroscope. There is also a small amount of secondary rays produced by the rays striking the various parts of the apparatus; these, however, do not affect the results since they come from all different parts of the vessel, and are therefore deflected very unequally.

When the electric or magnetic fields were applied in the same directions as in the case of the primary rays the same phenomena were observed; a gradual increase of ionization to a maximum with increasing fields, in one direction, and a decrease at once with the field in the other. The same absorbing layers were used in this case as in that of the primary rays. It was found that no increase of ionization above thirty layers of paper could be observed, that thickness being sufficient to almost completely absorb the secondary rays. These results confirm the idea that the secondary rays have a less penetrating character than the primary, and travel at lower speeds.

In order to estimate how far the rays were bent in the electric and magnetic fields the same method was used as for the primary rays. All that was necessary to do was to shift the tube of radium from beneath the slit in the lead box to one side so that no primary rays could get out. The soft iron screen was placed so that the rays were shielded from the influence of the field until they had passed the top of the zinc plate. The distance from the top of the zinc plate to the electroscope was less than in the case of the primary rays, but the width of the opening in the electroscope the same. The value of mV/e for no absorbing layer was found to be 1.56×10^3, and for an absorbing layer of 6 sheets of paper was 1.85×10^3. These values are about the same as the corresponding ones found for the primary radiation, and show that the lower limits in the latter case were those of the secondary rays. The upper limit for the secondary rays by this method was also the same as by the other method, viz., 30 layers of paper.

Substituting these values of mV/e in the results obtained by the first method we obtain 1.29 cm. as the distance through which the rays were deflected.

In this experiment, $l = 8.4$ cm., $h = 5.5$ cm., and $d = 17.3$ cm., and therefore,

$$V = \frac{2 \times 8.4 \left(\frac{8.4}{2} + 5.5\right)}{17.3 \times 17.3} \frac{X}{H} = 0.544 \frac{X}{H}.$$

In the accompanying table (VII) are expressed the final results obtained for the secondary rays.

TABLE VII.

Absorbing Layer.	$X_{(max.)}$	$H_{(max.)}$	mV/e	V cm./sec.	e/m
0			1.56×10^3		
6 paper.	6.9×10^{11}	16	1.85×10^3	2.35×10^{10}	1.27×10^7
14 "	7.5×10^{11}	17	1.97×10^3	2.40×10^{10}	1.21×10^7
22 "	8.5×10^{11}	18.5	2.16×10^3	2.50×10^{10}	1.16×10^7
30 "	9.6×10^{11}	20.2	2.36×10^3	2.58×10^{10}	1.09×10^7

It will be seen at once from this table that the values of the velocity, and ratio e/m, for the secondary rays are in good agreement with those obtained for the primary. Since the experiments on the secondary radiations from different substances, described earlier in this paper, showed that they were all deflected in a magnetic, and since further that the penetrating power of the rays were not greatly different, we can conclude that both metals and dielectrics give off when struck by β-rays, negatively charged particles with velocities, and ratio e/m, the same as those for the less penetrating β-rays.

As to the origin of these secondary and tertiary radiations, two possible explanations can be given. They might be the primary β-particles reflected back from the molecules of the bombarded substance. The other, and to me, more probable view is, that the secondary radiations are produced when the primary β-rays, striking the atoms of the substance, cause them to give off one or more of the electrons of which they are composed, with sufficient velocity to escape from the substance. The longer the path, and the greater the number of atoms which a β-particle encounters before it is absorbed, the greater will be the amount of the secondary radiation produced. The nature and amount of the secondary radiations produced will depend on the nature of the atom of the substance and on the density. The production of secondary and tertiary radiations is then similar in many respects to the production of β-rays by the radioactive substances; in the latter case the action is as far as we know spontaneous, in the former it is due to external agents.

CONCLUSION.

It will perhaps be instructive to briefly summarize here the main facts brought out in the present investigation.

The difficulty experienced at first in obtaining an electrostatic deflection of the β-rays can be shown to be due mainly, I think, to the disturbing action of the secondary and tertiary radiations.

When this disturbing action had been eliminated by the later methods adopted, values of the velocity, and ratio e/m, were obtained which agreed closely with those found by Kaufmann using an entirely different method.

The greater part of the secondary radiations, which are produced when the primary β-rays strike upon an absorbing material, are composed of negatively charged particles travelling at speeds nearly equal to that of the β-rays themselves, and having the same ratio e/m for corresponding velocities. The secondary rays themselves when incident upon a substanee produce tertiary rays, which are of slightly less penetrating character, are deflectable in a magnetic field in the same direction as the secondary and primary β-rays, and are probably of the same nature as these.

The values of e/m obtained for both the primary and secondary β-rays showed that the apparent mass of the particles increased as that speed approached the velocity of light.

Taking for granted that the assumptions involved in the calculations of the velocity, and e/m, are correct, my results together with those of Kaufmann furnish evidence in favor of the view that the mass of the electron is entirely electrical in nature.

In conclusion I wish to express my sincere thanks to Professor Ames for his kindly interest, valuable suggestions, and for the facilities which he placed at my command during the progress of this investigation.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
March, 1906.

LIMITATIONS OF THE BALLISTIC METHOD FOR MAGNETIC INDUCTION.

By A. Hoyt Taylor.

THIS investigation is incidental to a more extended inquiry into the magnetic properties of electrolytic iron — an inquiry made possible by a grant from the Carnegie Institution to Professor C. F. Burgess, of the department of applied electrochemistry, and by the kindness of the latter in furnishing the samples of iron tested.

Very early in this investigation it became apparent that the step by step ballistic method applied to an electrolytic iron ring, gave results which were very far from being in accord with those obtained by the method of reversals. It also developed that this discrepancy, although more pronounced in the case of pure electrolytic iron, was present, in varying degrees, in nearly all samples of iron and steel available for the test. It therefore seemed worth while to investigate these discrepancies, with a view to determining their possible quantitative effect on cyclic curves of magnetization, and with the object of devising a means of eliminating them.

An examination of the literature concerning the magnetic properties of iron is too great an undertaking to be attempted in detail. It is quite evident, however, that this effect has not escaped notice. Ewing[1] notes that there are slow changes in the magnetic induction taking place some time after the field has reached a steady state, and remarks that these would cause an error where a ballistic method is used. E. Wilson[2] working with "almost pure iron" found large discrepancies between the results obtained by the method of reversals and by the step by step method.

He showed that the error came in principally in the steep parts of the hysteresis loop and that it was not a function of the time constant of his primary circuit, but was due rather to a viscous time lag

[1] Magnetic Properties of Iron, etc.
[2] Proc. Roy. Soc., 62, 1898.

of the magnetic induction behind the field. This time lag he showed was persistent and noticeable for as long as ten seconds after the changes in field strength had been made, and was of such magnitude that it could not be accounted for on the basis of the retarding effect of eddy currents. He did not vary the time constant of his circuit within very wide limits, nor did he investigate the effect of changing the period of his galvanometer. His results can hardly be extended so as to find the distortion produced in the hysteresis loop by these errors.

R. Jouaust [1] found viscous hysteresis in many soft steels, the extent of viscosity depending somewhat on the dimensions of the rings tested. He suggests that the step by step method be so modified that in running a hysteresis loop the steps be always taken from low fields to comparatively strong ones. This would eliminate magnetic viscosity, which is not evident under strong fields, but would require a rather complicated cycle of operations between observations.

Fr. Rücker [2] notes magnetic viscosity in iron and steel, and states that the step by step method gives values for the magnetic induction which are too low. I have not access to this paper, but according to a brief review of the same, no remedy for the error is suggested.

In the present case, when discrepancies were observed between the method of reversals and the step by step method, the author was at first inclined to ascribe them to peculiarities of the electrolytic iron. An investigation of two samples of laminated soft iron rings, made from armature stampings showed the same effect, though not in so marked a degree. Then two solid iron rings which had been used in the laboratory for testing purposes were tried, both showing the effect to a considerable extent. In the case of one laminated iron ring, of one square inch cross-section, with a radius of five inches, and having 1,009 turns on the primary, the method of reversals gave values for the maximum induction 47 per cent. higher than those obtained by the step by step method. This was found to be due to the fact that in certain portions of the cycle where the differential permeability was high and hence the self-induction

[1] Comptes Rendus, Vol. 139, pp. 272, 1904.
[2] Diss. Halle, 1905.

of the primary circuit was large, the time constant of the primary circuit was so large that the primary current, and hence the field strength, did not attain to its maximum value until after the first throw of the galvanometer had taken place. The time constant of the circuit was unusually large because the resistance was low and constant, variations in primary current being made by varying the applied voltage over any desired range with a potentiometer device. This scheme was exceedingly convenient and easy of manipulation by one observer working alone, but was dropped for the reasons cited above. When a constant potential and a variable series resistance is used in the primary circuit, then at points where the differential permeability, and hence the inductance, of the primary circuit is high, the field is always low, the primary current small, and hence the series resistance large. This gives a small time constant, and an applied voltage (20 volts) was found such that any error due to slow rise of primary current was eliminated for all of the rings. This was shown by the fact that doubling the applied voltage and series resistance, hence halving the time constant, did not affect the results. In the case of all samples except one, which was hard iron with a rather large coercive force (4.00 dynes), there was still a very considerable discrepancy between the maximum induction as obtained by the two methods, the method of reversals giving invariably the greater value. In the case of the electrolytic iron, which after annealing behaves as far as I can say at present, like any soft steel, the effect was most marked, the discrepancy amounting to 17 per cent. This is undoubtedly due to magnetic viscosity, and an attempt was made to eliminate it by increasing the galvanometer period from 5.5 to 15.0 seconds. By this means the maximum inductions as determined by the two methods, were brought within 11.05 per cent. of each other. From this one may infer that the viscous effect is of such long duration that no galvanometer of sufficiently short period to be workable, would give results very nearly correct. An instrument of the fluxmeter type would be admirably suited to such cases.

However, the step by step method may be so modified as to prevent these errors from being additive, and to nearly eliminate them, even with a fairly short period galvanometer. The arrangement of

the apparatus is nearly the same as for the regular step by step method. The secondary coil of the ring being tested is connected in series with the galvanometer G, a suitable high resistance H, and a switch S_4. A damping coil and commutator, not shown in the sketch, were also included in this circuit.

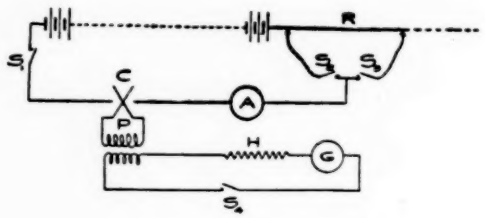

Fig. 1.

The primary coil P is connected through a commutator C and switch S_1 with a storage battery and an ammeter. The switches S_2 and S_3 allow more or less of the wire rheostat R to be put in circuit. If desired (as in the step by step method) one of the switches S_2 and S_3 may always be kept closed, and hence the current never broken. The rheostat R consists of I. A. wire, mostly No. 30, but with five or six ohms of No. 16 for the larger currents. The switches S_2 and S_3 connect with the rheostat by means of flexible leads and spring clip terminals, provided with copper jaws for gripping the rheostat wire firmly.

For the determination of points on the upper branch of the hysteresis loop, from saturation point to retentivity point (zero field) the method is as follows: S_1 is closed and S_2 is connected to such a point on R that a current flows in the primary, strong enough to produce a saturation field. In this case the current was 5.00 amperes and the field 100 dynes, which was in most cases far more than enough to cause saturation. Then S_3 is closed, connected to such a point on R that when S_2 is opened, the current falls to any desired valve. Then S_4 is closed and the galvanometer brought to rest with the damping coil. Finally, on breaking S_1, one observes the deflection caused by the change in induction in passing from any desired point such as A, for instance, in Curve I., to O, the retentivity point.

The observations may be repeated as often as desired, the cycle of operations being this: Open S_4, close S_1, close S_2, close and set on the rheostat S_3, open S_2, open S_1. Whatever viscous effect may be present will not cause a cumulative error as in the regular step by step method.

For the remainder of the cycle, from the retentivity point to the saturation point the change of induction is observed from the reten-

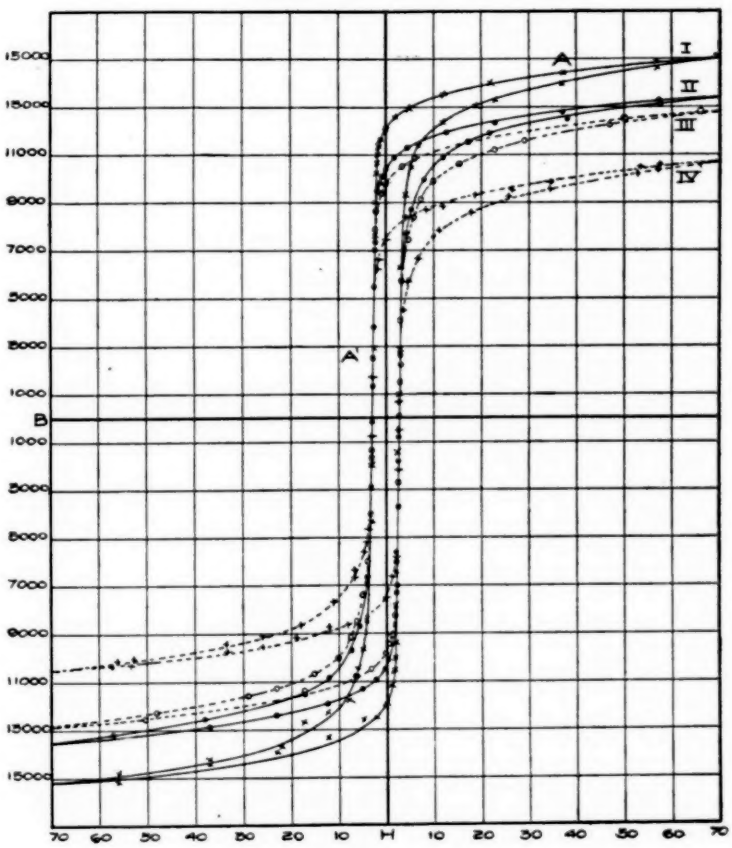

Fig. 2.

tivity point to any point, such as A', Curve I. This requires a slightly more complicated cycle of operations, since the iron must be carried back to the first or upper saturation point, and down to the retentivity point before the observation is taken. S_3 is set on

the rheostat for the current corresponding to the field strength at A'. The method is then as follows: Open S_4, reverse C, close S_2, close and set S_3, open S_2, open S_1, reverse C, close S_4 and close S_1, observing the deflection.

Curve I. was obtained in this manner, and represents what we may call the true hysteresis curve for a ring of annealed electrolytic iron of radius 4.12 cm. and area 0.7 cm.^{2}, primary winding 424, secondary 700. The period of the shielded ballistic galvanometer used was 15 sec. and the applied voltage in the primary circuit was 40 volts.

It required nearly twice as much time to run this test as it did to get Curve II., using the same apparatus and the regular step by step method. The hysteresis area of Curve II. is 18 per cent. smaller than that of Curve I.; the retentivity point is 16 per cent. lower, and the maximum induction is 11.8 per cent. lower. The coercive force is practically the same for all four curves.

Curve III. was taken exactly as was Curve II., except that the galvanometer period was 5.5 sec. and hence the viscosity causes a larger discrepancy.

Curve IV. was taken exactly as was Curve III., except that the primary resistance was kept constant and the voltage varied by a potentiometer arrangement in order to vary the primary current. As explained earlier in the paper, this gives a larger time constant and introduces another error besides the one due to viscosity.

These discrepancies are more marked as more and more steps are taken on the curves, because the errors are cumulative. They are not peculiar to electrolytic iron, but may occur in any soft steels, and in many samples of iron, even when laminated, although perhaps not to so marked a degree.

It seems clear then, that the ring tests should be done with the modified ballistic method, or better yet, if sufficient sensibility can be obtained, with an instrument of the fluxmeter type.

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THE THERMO-ELECTRIC BEHAVIOR OF SILVER IN A THERMO-ELEMENT OF THE FIRST CLASS.

By W. D. Henderson.

Introductory.

THE research recorded in the following pages has for its object an investigation of the thermo-electric behavior of silver, with special reference to the more general problem of the relation of heat to electromotive force. Throughout the work, three subsidiary problems have been kept in view — namely, (*a*) an investigation of the direction of the electromotive force due to a difference of temperature; (*b*) an investigation of the relation of the electromotive force due to a given difference of concentration, to that due to a corresponding difference of absolute temperature; and (*c*) an investigation of the relation of thermo-electromotive force to the concentration of the electrolyte.

For the sake of clearness in the use of terms, the following explanatory paragraphs are given:

Two electrodes of a given metal immersed in a solution of the salt of this metal, constitute a reversible element of the simplest type. Consider the cell to be of the ordinary U-form, and let the two limbs of the cell, and also the two electrodes contained therein, be represented by the symbols A and B. Also, the cathode is that electrode *to* which the current flows in the electrolyte, or *from* which the current flows in the external circuit. A concentration cell, of the form described above, is one in which the concentration of the electrolyte in A differs from that in B; a thermo-element is one in which the concentration is the same in both limbs, but the temperature in A differs from that in B. An element of the first class is a cell in which the two electrodes are of the same metal, and are immersed in a solution of a salt of this metal.

Now, it is a well known fact that a difference of electromotive force may be established between the electrodes A and B in at least two ways. First, an electromotive force will result from a difference of concentration at A and B, the temperature on the two sides being the same; and second, an electromotive force will result from a difference of temperature at A and B, the concentration on the two sides being the same. An electromotive force due to a difference of temperature will be referred to as a thermo-electromotive force.

HISTORICAL.

As early as 1825 Walker[1] experimented on the relation of heat to electromotive force. He was followed by Faraday,[2] and later by Gore.[3] All three in general used platinum electrodes, hence their results were vitiated by polarization effects. In the few cases in which electrodes of the same metal as the salt in solution were used, complex chemical reactions seriously interfered with definite results.

In 1880 Bouty[4] reported a series of tests in which he used as electrodes a number of metals immersed in solutions of their own salts. For copper, zinc, cadmium, and mercury, the warm electrode was the cathode; for iron the results were very erratic; for gold the direction of the current changed for different temperatures; for silver, nickel, magnesium and aluminium the results were variable and unsatisfactory, the cold electrode, in general, being the cathode. He concluded that the electromotive force is proportional to the change in temperature and is independent of the concentration.

Carhart[5] confirmed Bouty's results for copper and zinc, but found that the electromotive force is not independent of the concentration. His researches with reference to the change of electromotive force with change of concentration were later confirmed by Ebling,[6] who worked on cells of the type, Cu — $CuSO_4$, Zn — $ZuSO_4$, Cd — $CdSO_4$.

[1] Pogg. Ann., 4, 327, 1825.
[2] Exp. Researches, Sr., 17, 225, 1932, 1840.
[3] Proc. Roy. Soc., 1856, and following.
[4] J. de Phys., 9, 1880; Comp. Rend., 90, 918, 1880.
[5] Carhart's Primary Batteries.
[6] Wied. Ann., 30, 130, 1887.

Nernst,[1] using mercury electrodes in a thermoelement of the type, $Hg - Hg_2Cl_2 - HCl - Hg_2Cl_2 - Hg$, found the warm electrode to be the cathode.

In 1894 Hagenbach[2] repeated the experiments of both Bouty and Ebling. His results for copper, zinc and cadmium agreed well with those of Ebling. In many particulars, however, his results did not agree with those of Bouty. For example, in the case of $Ni - NiSO_4$, Bouty reported that the cold electrode was the cathode. Hagenbach repeated the experiment, and reported that no definite results were attainable. He also reported that silver electrodes in solutions of silver salts gave unreliable results.

In connection with his thermo-electric theory of concentration cells, Carhart[3] investigated the electromotive force of cells of the following types: $Zn - ZnSO_4 - Zn$, Zn Amal. $- ZnSO_4 -$ Zn Amal., $Ni - NiSO_4 - Ni$. He called attention to the relation between the concentration of the electrolyte and the thermo-electromotive force, and also its import when applied to the Helmholtz equation for electromotive force.

McClellan[4] in 1903, and Meyer[5] the following year, worked on the problem of the thermo-electromotive force of nickel nitrate. Both, however, used platinum electrodes, hence obtained unsatisfactory results due to polarization effects.

It may be noted in this connection that the Peltier effect, both at the surface of contact of a metal and a solution, and at the surface of separation of two electrolytes, has been measured by a number of investigators,[6] who have shown that in general the same laws appear to hold as in the case of metals.

Discussion of the Problem.

The Gibbs-Helmholtz equation for electromotive force is based on fundamental principles of thermo-dynamics; the Nernst equa-

[1] Zeit. f. Phys. Chem., 4, 169, 1889.

[2] Wied. Ann., 53, 1894.

[3] Trans. Am. Electrochem. Soc., 1, 1, 1902; 2, 123, 1902.

[4] Phys. Rev., 17, 255, 1903.

[5] Phys. Rev., 19, 156, 1904.

[6] (*a*) Pogg. Ann., 13, 467, 1870; (*b*) Wied. Ann., 9, 573, 1880; (*c*) Ann. de Chim. et Phys., (7), 3, 83, 1894.

tion is derived from the conception of solution pressure and osmotic pressure as applied to the electrode and electrolyte of a cell. The former is, mathematically speaking, the more rigid of the two; the latter, however, lends itself, within certain limits, more readily to experimental demonstration. In the Nernst equation the electromotive force is expressed as a function of the solution pressure of the metal, the osmotic pressure of the solution, and the temperature. It assumes the application of the gas laws, and takes no account of sources of electromotive force other than those mentioned above. A general expression of this equation is as follows:

$$E = \frac{R}{Kn}\left[T_1 \log \frac{P_1}{p_1} - T_2 \log \frac{P_2}{p_2} + T_3 \frac{u - v}{u + v} \log \frac{p_1}{p_2}\right]. \qquad (1)$$

E represents the resultant electromotive force of the cell; T, absolute temperature; R, the gas constant; K, 96,540 coulombs; n, valence; P, solution pressure of the metal; p, osmotic pressure of the solution; u and v, migration velocities of the ions.

When $P_1 = P_2$, and $T_1 = T_2 = T_3$, equation (1) may be written

$$E = \frac{RT}{Kn}\left[\frac{2v}{u + v}\right] \log \frac{C_1}{C_2}, \qquad (2)$$

in which the ratio of concentrations, C_1/C_2, is set equal to the ratio of osmotic pressures, p_1/p_2.

Nernst has proved that under certain conditions, as in the case of $Ag - AgNO_3$ concentration cell, the calculated values, obtained by means of equation (2), agree remarkably well with the observed values.

Now, the question arises, how far can this proof be extended under other conditions of the variables T and p? That is to say, how far, for example, will the conception of solution pressure and osmotic pressure, as applied to the concentration cell, explain the phenomena of a thermo-element of the first class?

The results of investigation thus far, with respect to the relation of heat to electromotive force, may be collected under three heads as follows: First, work done with polarizable electrodes; second, work done with unpolarizable electrodes in cells of the second class — that is, cells of the type, $Hg - Hg_2Cl_2 - HCl - Hg_2Cl_2 - Hg$;

and third, work done with unpolarizable electrodes in the cells of the first class — namely, of the type, $Zn - ZnSO_4 - Zn$. It is to phenomena connected with cells of the last named group that this paper invites attention, since in cells of this class are found the simplest possible conditions and the fewest disturbing factors.

The writer is perfectly well aware that the mere tabulation of data does not offer a solution to the problem. Before such data can be of much value we must have pretty definite information regarding the physical condition of the electrodes, the nature of the electrolyte, and what occurs when these component parts of the cell are combined. If, for example, the electrodes are oxidized, or contain occluded gases, or become polarized, variable and unsatisfactory results will necessarily follow. Or, again, if in the case of the electrolyte, unknown and complex physical or chemical changes occur in the process of solution, little can be expected in the way of definite results.

Assuming now that the above-named conditions can be fairly well satisfied, let us consider for a moment the relation of E to the variables T and p (absolute temperature and osmotic pressure). If in the U-shaped cell previously mentioned the electrolyte be of uniform concentration, and the electrode A be brought to a temperature higher than B, then p in limb A will be greater than that in limb B, since the osmotic pressure varies as the absolute temperature. Then, assuming that the solution pressure, P, does not change, and assuming also that no other factors enter in, the resulting electromotive force will be directed *in the electrolyte* from the cold electrode to the warm; that is to say, the warm electrode will be the cathode. If, however, the cold electrode prove to be the cathode, then it will be necessary to revise our assumptions, or look for other factors as a source of electromotive force, in addition to those already named.

Also, since E is a function of p, and p in turn is a function of both T and C, it is possible to vary p, and therefore E, by varying either the absolute temperature T, or the concentration C.

Now, if the conditions be chosen such that T_1 (equation 1) be equal to T_2, and p be varied through a series of values, y_1, y_2, etc., by making C_1 greater or less than C_2, a resultant electromotive force, E',

will be observed in accordance with the well-known laws of the concentration cell. Suppose, further, that C_1 be made to equal C_2 (equation 2) and p be varied now through a calculated series of values, p_1, p_2, etc., as above, by making T_1 greater or less than T_2, again there will result an electromotive force, say E''. How will E'' compare with E', previously obtained? Theoretically, the two values should be the same. In case a difference in value between E' and E'' be found, and such difference be greater than that due to experimental error, then again we must revise our assumptions, or look for some additional factor as a source of electromotive force.

Then, to summarize, in considering an element of the first class in connection with the subject of the relation of heat to electromotive force, three important questions arise. First, do all metals immersed in solutions of their own salts, under conditions as described, give a current through the electrolyte from the cold to the warm portion — that is, is the warm electrode the cathode? Second, how does the electromotive force resulting from osmotic pressure changes, due to a given difference in concentration, compare with the electromotive force resulting from osmotic pressure changes, due to a corresponding difference in absolute temperature? And third, in a thermo-element, what is the relation between the concentration of the electrolyte and the resulting thermo-electromotive force? In other words, to summarize all three questions, under varying conditions of the temperature, will the factors of solution pressure and osmotic pressure account for the observed electromotive force?

The answer to these questions involves the working out of a large and complex problem, the solution of which requires much more extended research than comes within the limits set for this paper. The following investigation has to do mainly with the thermo-electric behavior of silver, and has been prosecuted with the hope that some further light may be thrown on the general problem of the relation of heat to electromotive force.

APPARATUS.

The following is a brief and general description of the apparatus used, special pieces, such as electrodes, etc., being described later in connection with the experiments.

Two thermostats were employed, and are shown in outline in Figs. 1 and 3. Temperature measurements were made by means of Beckmann thermometers, reading directly to hundredths of a degree.

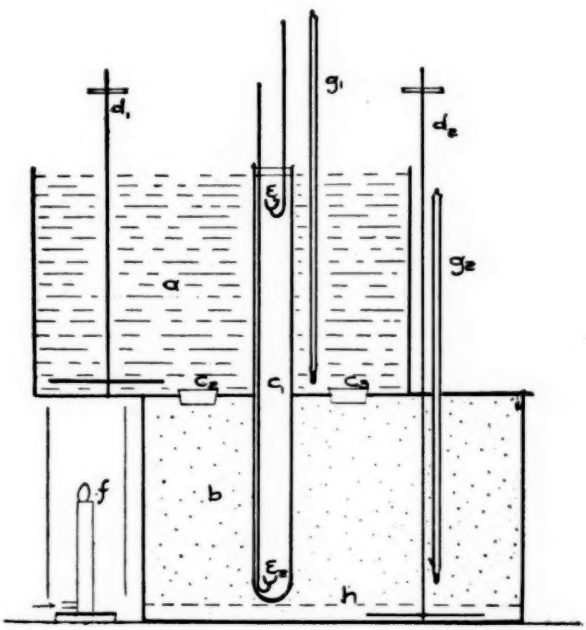

Fig. 1.

The temperature in the warm bath was held constant to within a few hundredths of a degree by means of large toluene-mercury regulators. In the thermostat shown in Fig. 1, the ice bath was in the lower chamber; in the case of that shown in Fig. 3, the ice bath consisted of a large Dewar flask enclosed in a jacket of building. felt. In the thermostat shown in Fig. 1, a stirrer was used in both chambers; in that shown in Fig. 3, a stirrer was used only in the warm bath.

Measurements of electromotive force were made by means of an Otto Wolff potentiometer which reads directly to 0.00001 volt. A Leeds and Northrup galvanometer was employed of such sensitiveness that a change of 0.00001 volt gave a deflection of one scale part, at a distance of ten feet. The electromotive force to be measured was balanced against that of a standard cadmium cell.

EXPERIMENTS AND RESULTS.

A preliminary test was made with reference to the direction of the electromotive force of a number of metals when immersed in solutions of their own salts. A large H-formed cell was employed, the cross-tube of which contained a stop-cock. During the test, one leg of the cell was kept in a 25° bath; the other, in ice. The following types of reversible cells were used: $Zn - ZnSO_4 - Zn$; $Cd - CdSO_4 - Cd$; Cd Amal. $- CdSO_4 -$ Cd Amal.; $Hg - HgNO_3 - Hg$; $Ag - AgNO_3 - Ag$.

In the case of zinc, cadmium, cadmium amalgam and mercury, the warm electrode was the cathode; in the case of silver, the cold electrode was the cathode.

A more pretentious piece of apparatus was now constructed, and a more thorough investigation of the direction of the electromotive force of silver undertaken. Fig. 1 represents in outline the containing baths, cells, and auxiliary apparatus. The warm bath (a) was kept at a temperature of 25°; the cold bath (b) about zero. Cell (c_1) consisted of a cylindrical glass tube 60 cm. in length, and about 5 cm. in diameter. Two stirrers were provided, d_1 and d_2, the latter working in the cold water below the ice. The flame (f) was controlled by a regulator not shown in the cut. It was easily possible to hold the temperature constant in either bath to within a few hundredths of a degree. It may be well to remark here that this particular piece of apparatus was devised with two objects in view — namely, (a) the investigation herein described, and (b) an investigation of the so-called Soret phenomenon, for the accomplishment of which the apparatus is admirably adapted. Openings between the chambers (a) and (b), Fig. 1, were provided for five cells similar to (c_1), three such being shown in the cut.

The electrodes (E_1) and (E_2) deserve special mention. At the beginning of the work great difficulty was experienced in getting electrodes that would give anything like zero initial values. What was required were electrodes that would give zero readings to nearly the fifth decimal place, and second, electrodes that would give reproducible and constant values for several days or weeks. As already stated, unusual difficulties were met with in attempting to fulfill these conditions. Electrodes prepared from the same piece

of metal, under apparently the same conditions, would sometimes give an initial electromotive force of as high as 0.003 to 0.005 volt. And again, after electrodes were obtained that would give the required initial reading, it was found that they would not remain constant for any length of time, going now to positive values, and again to negative, in a most hopeless and discouraging manner. In view of the difficulties just mentioned, it is not at all surprising that Bouty and Hagenbach spoke of silver as "variable" and "unreliable."

The first difficulty encountered was in sealing the electrode to the glass supporting tube. In a few cases it was possible to seal fine silver wire directly into the glass, but in most cases this failed. After a test extending over a period of two or three months, all methods of sealing in with wax in any form were abandoned. Such electrodes in a solution of silver nitrate invariably "broke down" — that is, they eventually gave erratic and variable results, due to the action of the solution upon the wax. Electrodes prepared by depositing, electrolytically, silver on clean platinum spirals gave fairly good results, so far as constancy was concerned, but it was found that two sets of electrodes prepared in exactly the same manner, and immersed in the same solution would often give widely different results.

The electrodes finally made use of were prepared after the following manner: From the purest obtainable chemicals, silver chloride was precipitated. The chloride was filtered out, washed and then dissolved in ammonium hydroxide, and from this solution the silver was precipitated by means of pure electrolytic copper. The precipitated silver was now digested in excess of ammonia, after which it was thoroughly washed. The final product consisted of a fine grayish powder, which will be referred to hereafter as "precipitated silver." The complete form of this electrode is shown in Fig. 2. The precipitated silver, just described, was placed in the cup (j). A long silver wire (m) was fused to a short platinum wire (k) at (l). The platinum wire, in turn, was fused through the glass as shown, the point which protruded into the cup (j) being silver plated, thus making electrical contact with the metal of the electrode proper. In one case, hereafter mentioned, no platinum

wire was used, the silver wire (*m*) being fused through the cup at (*j*). With such electrodes, except that the form was modified later on, all the results recorded with reference to silver were obtained. It was found possible to obtain zero initial readings to nearly the fifth decimal place, and further, not only did different sets of electrodes give concordant results, but the values showed remarkable constancy over a relatively long period of time.

Nothing new is claimed for the above method for the preparation of silver, or for the use of finely divided metal as an electrode.[1] The details are given because, of the many methods suggested, the foregoing gave the most satisfactory results.

Cell (*c*) (Fig. 1) was now filled with a tenth normal solution of silver nitrate. Both electrodes (ϵ_1) and (ϵ_2), were placed near the top of the cell (Tem. 25°), and the initial electromotive force observed. Electrode (ϵ_2) was then lowered to the bottom of the cell (Tem. near 0°), and observations were taken over a period of twenty days.

The object of this test was threefold, namely (*a*) to note the direction, (*b*) the constancy, and (*c*) the conditions attending the resulting electromotive force over a considerable period of time.

The results of the test are embodied in Table I.

In considering Table I., it is to be noted that the cold electrode remained the cathode throughout the experiment, and that the electromotive force was remarkably constant. Further the elimination of oxygen from the electrolyte by exhaustion, and then saturating the solution with nitrogen, seemed to produce no notable change in the values observed. After exchanging the electrodes, the electromotive force was 0.00030 volt higher than before the change. This small difference might be accounted for by the fact that at the close of the experiment it was found that one of the glass tubes of the electrodes was slightly cracked, allowing a little of the solution to come in contact with the silver wire (*m*) (Fig. 2).

It was now thought desirable to repeat the experiment recorded in Table I., and to extend the test to other metals. The object here was to compare silver, mercury, and cadmium amalgam under similar conditions, and also to see if the "Soret effect" entered into the problem. By the "Soret effect" is meant the production of a

[1] Richards and Lewis in Zeit. f. Phys. Chem., 28, 8.

TABLE I.

Date.	$T_1 - T_2$	E.M.F.	Notes.
Feb. 25, 8 A. M.	0.0	0.00006	Initial condition of electrodes. Bath at 25°. Electrode *A* at top. Temperature = 25°. Electrode *B* at bottom. Temperature = 0°.
" 25, 11 "	24	966	Cold electrode cathode (+).
" 25, 8 P. M.	23.75	961	
" 26, 8 "	23.5	960	
" 27, 8 A. M.	23.9	963	
" 27, 12 "	23.7	965	
" 28.	23.5	966	
March 1.	23.3	967	
" 2, 8 A. M.	23.5	965	
" 2, 1 P. M.	23.6	968	
" 2, 9 "	23.7	966	
" 3.	23.6	964	The electrodes were now exchanged — electrode *A* was put at bottom; *B* at top. *A* changed from — to +; that is, the cold electrode again became the cathode.
" 3.	23.7	0.00130	
" 4.	23.6	1071	
" 5.	23.8	1045	
" 6.	23.6	1022	
" 7.	23.7	1002	
" 8.	23.7	977	Had trouble here with motor; water in bath not well stirred.
" 9.	23.6	977	
" 10.	23.7	975	
" 10, 2 P. M.	23.8	990	From this time on the solution in the cell was saturated with pure nitrogen.
" 10, 9 "	23.7	993	
" 11.	23.6	998	
" 12.	24.5	980	
" 13.	23.6	991	
" 14.	23.8	992	
" 16.	23.7	995	
" 17.	23.9	998	

difference of concentration in the cell due to the difference in temperature. The solution at the top of the cell (c_1), Fig. 1, was at a temperature 25° higher than that at the bottom. This difference of temperature would produce, at the outset, a corresponding difference of osmotic pressure, the greater pressure being at the top. According to the theories embodied in an explanation of the Soret phenomenon,[1] however, equilibrium in the cell would eventually be

[1] Ann. de Chim. et Phys. (5), 22, 293, 1881.

established by an osmotic pressure at the bottom of the cell (the cold portion) due to an increase of concentration, equal to that at the top, due to the increase of temperature. In other words when the contents of the cell came to equlibrium, the solution should show an increase of concentration at the bottom (the cold portion) proportioned to the difference of absolute temperature between the two extremities of the cell.

Two new cells (c_2 and c_3), Fig. 1, were now put into the bath in a manner similar to that of c_1. The three cells were of the following types: $Ag - AgNO_3$; Cd Amal. $- CdSO_4$; $Hg - HgNO_3 + HNO_3$.

The silver electrodes were similar to those described in connection with Table I. In this case no platinum wire was used in the construction of the electrode, the silver wires being fused into the glass at (k), Fig. 2. Long wires were used to avoid any possibility of a thermo-electromotive force of metallic contact.

The cadmium amalgam electrodes were, in outline, similar to that shown in Fig. 2. In this case, however, the cup (j) was filled with twelve and a half per cent. cadmium amalgam. The tube (i) was also filled with amalgam, which made electrical contact with (j) by means of a short platinum wire (k). The platinum wire was so short that there was no possibility of a resultant electromotive force of metallic contact, since in both electrodes there could be no difference of temperature at the ends of the wire.

Fig. 2.

The mercury electrodes were prepared in a similar manner.

In the case of the electrolyte, a tenth normal solution was used in each of the cells. Just enough nitric acid was added to the mercury cell to hold the mercurous nitrate in solution.

After the experiment had been in operation seven days, analyses for concentration changes at the electrodes were made several times a day. By means of a long capillary pipette a small quantity of the electrolyte of a given cell was drawn off from the cold and the warm portions, and tested for concentration changes by conductivity methods.

A record of the experiment follows in Table II.

TABLE II.

Date.	$T_1 - T_2$	*Ag* Cold El. +	*Cd Amal.* Hot El. +	*Hg* Hot El. +	Notes.
May 20	0.0	0.00008	0.00012	0.00000	Both electrodes at 30°.
" "	29.95	1105	1184	340	
" 21	30.00	1234	1157	338	
" "	30.00	1264	1162	350	
" 22	29.97	1270	1163	352	
" 23	30.02	1278	1173	363	
" 24	30.03	1278	1176	366	
" 25	30.01	1279	1174	364	
" 26	30.00	1284	1168	368	
" 27	29.90	1276	1179	368	Analysis was begun here.
" 28	29.92	1266	1183	374	
" 29	29.97	1278	1194	372	
" 30	30.00	1281	1195	384	

Analyses during the progress of the experiment recorded in Table II. showed no changes of concentration at the electrodes — in other words, showed no evidence of the Soret phenomena. This was probably due partly to the length of cell used (60 cm.), and also to the fact that sufficient time had not elapsed for such a change to make itself manifest. A further investigation of the Soret phenomenon will be made with the apparatus just described and shown in outline by Fig. 1.

In the case of silver, the cold electrode remained the cathode. For cadmium and mercury the warm electrode was the cathode.

Silver and cadmium gave remarkably constant values.

A careful investigation was now begun with reference to the physical character of the electrode in the case of silver. The test was qualitative in character and included cells of the types, $Ag - AgNO_3$; $Ag - AgClO_4$.

The large H-form cell, used in the preliminary tests, was employed. One leg was kept at a temperature of 25° ; the other at the temperature of the ice bath. After each test the electrodes were reversed with respect to the warm and the cold sides of the cell and new readings taken.

The silver wire described in the tests was prepared as follows: Silver was deposited electrolytically, and the product was fused and run into sticks, which in turn were drawn into wire. This wire when freshly drawn was very brittle, but when slightly annealed became very soft and pliable. The other forms used were (*a*) silver deposited on platinum, (*b*) silver cleaned in dilute nitric acid, (*c*) precipitated silver, as previously described.

The conditions, under which the tests were carried out, and the results are given in Table III.

TABLE III.

Test No.	Condition of Electrode.	Result.
1	Freshly drawn silver wire—Unannealed—Brightly polished.	Cold electrode, cathode.
2	Freshly drawn silver wire—Annealed in Bunsen flame—Brightly polished.	" "
3	Freshly drawn silver wire—Annealed in an atmosphere of pure nitrogen by means of an electric current.	" "
4	Freshly drawn silver wire—Cleaned in dilute nitric acid.	" "
5	Silver deposited from tenth normal solution of silver nitrate on platinum spiral.	" "
6	Silver deposited on platinum spiral from standard cyanide silver-plating solution.	" "
7	Heavy deposit of silver, prepared as in (5), and cleaned in 50 per cent. solution of nitric acid.	" "
8	Precipitated silver, as previously described.	" "

It thus appears from the preceding tables that silver in a neutral solution of $AgNO_3$ or $AgClO_4$, as a thermo-element, gives for a difference of temperature between 0° and 30°, an electromotive force directed in an opposite sense to that of zinc, copper, cadmium and mercury.

The second part of the investigation was now taken up, namely, an investigation of the relation between concentration changes and corresponding temperature changes, in the production of electromotive force. As a preliminary step, a few tests were made with reference to the temperature coefficient of a concentration cell of the type, $Ag - AgNO_3 - Ag$. According to the formula used in

the calculation of the electromotive force of such a cell, the E.M.F. should vary directly as the absolute temperature, the difference in concentration remaining constant and the temperature being the same on both sides.

The H-form of cell, previously mentioned, was employed, and precipitated silver was again used as electrodes. No attempt was made to carry the experiment to any great length, it being required merely to show that under the conditions assigned, no abnormal changes occurred.

Summary of results given in Table IV.

TABLE IV.

Cell No.	C_1/C_2	Cond. of Electrodes.	Calc. E.M.F.	Obs. E.M.F.
1	5.260	Both electrodes at 30°.	0.04564	0.04500
1	"	Cell placed in ice bath. T. = 0.06°.	0.04149	0.04000
1	"	Cell again placed in 30° bath.	0.04564	0.04540
1	"	Cell again at 0.06°.	0.04149	0.04174
2	1.596	Temp. = 30°.	0.01291	0.01310
2	"	Temp. = 1.25°.	0.01174	0.01223
3	1.670	Temp. = 30°.	0.01408	0.01432
3	"	Temp. = 0.06°.	0.01282	0.01260

The apparatus used in this part of the work is shown in Figs. 3 and 4. The cell employed was of the three-legged form, two limbs (A_1 and A_2) being kept in the warm bath, the remaining limb (A_3) in the ice bath. A_1, A_2 and A_3 were connected by means of siphons each of which contained a stop-cock.

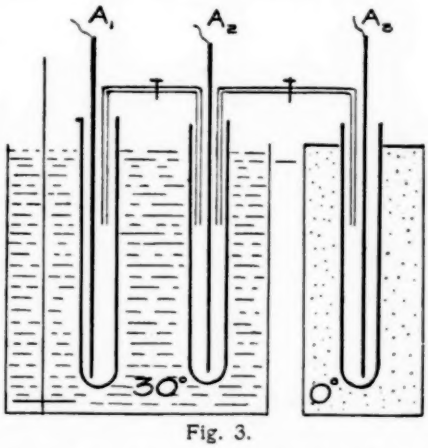

Fig. 3.

The method of procedure was as follows: A neutral tenth normal solution of silver nitrate was put into all three cells. Cells A_1 and A_2 combined were designed to act as a concentration element; cells A_2 and A_3 to act as a thermo-element. Due to the difference of temperature between A_2 and A_3 there resulted an electro-

motive force, the ratio of the absolute temperatures of the two sides being 303 : 273, or 1.11. With this combination the cold electrode was as usual the cathode. The next step was to vary the concentration in A_1 through a series of values, thus giving a series of E.M.F. readings due to the difference of concentration between A_1 and A_2. The object was to find what concentration ratio was required to produce an electromotive force equal to that due to an absolute temperature ratio of 1.11.

In the preliminary tests the electrodes used were prepared by electrolytically depositing silver upon platinum spirals. The results obtained with this form of electrode were not entirely satisfactory. In the final test in this case, and in all subsequent tests, the precipitated silver electrodes were used to the exclusion of all others.

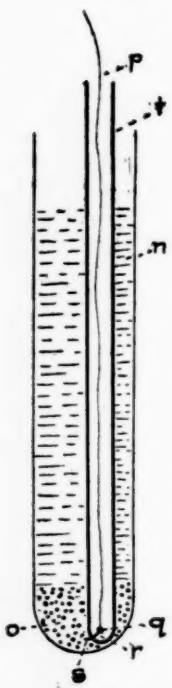

Fig. 4.

The form of electrode used in the final test is shown in Fig. 4. A long silver wire (p) was fused to a very short platinum wire (r), which in turn was sealed into the lower portion of the tube (t) in such a manner that the point (s) projected out of the side of the tube a few millimeters from the end. This was to prevent the silver-plated point (s) from being injured on the bottom of the cell.

To set up the cell, precipitated silver to the depth of one or two centimeters was put into each limb (A_1, A_2 and A_3). A given solution of silver nitrate was then added *and the contents of each cell thoroughly shaken.* The tubes containing the conducting silver wires were now put into the cell, as shown in Fig. 4, the silvered point (s) making electrical contact with the precipitated silver. The cells were now put into their respective baths and connected by means of the two siphons, as shown in Fig. 3.

A thermo-electromotive force at once resulted between A_2 and A_3, due to a difference of temperature of 30°. A_1 and A_2, on the other hand, being of the same temperature and concentration, were

in equilibrium to begin with. Now, as in the preceding test, the concentration in A_1 was varied through a series of values by the following method: After each reading the stop-cock between A_1 and A_2 was closed, and A_1 was taken from the bath. A small quantity of the electrolyte of limb A_1 was removed by means of a pipette, and a corresponding amount of water was added. The cell was then thoroughly shaken, the special form of electrode just described making this operation possible. This agitation of the electrode is quite necessary when it is desired to vary the concentration of the electrolyte through a series of values. Cell A_1 was now returned to its former position and allowed to come to the temperature of the bath.

The conductivity of the electrolyte in A_2 was taken once for all; that in A_1 was taken after each dilution. From this data the relative concentrations in A_1 and A_2 were obtained. The ratio $C_1 : C_2$, as used in the following table, represents a ratio of molecular conductivities. For each variation of the concentration in A_1 the value of the resulting electromotive force between A_1 and A_2 was calculated by means of equation (2), the data for the values of u and v being obtained from the Kohlrausch and Holborn tables. The object here of comparing the observed with the calculated values was to see how closely, under the conditions, the gas laws applied. In making the solutions described above, water prepared for conductivity purposes was used.

For tabulation of results of the foregoing tests see Table V.

TABLE V.

Comparison of the electromotive force due to a given difference of absolute temperature, with that due to a corresponding difference of concentration. For outline of cell, see Figs. 3 and 4.

C_1/C_2	T_1/T_2	Obs. E.M.F.	Calc. E.M.F.	C_1/C_2	T_1/T_2	Obs. E.M.F.
1.114	1	0.00284	0 00291	1	1.11	0.01408
1.388	1	.00813	.00910	1	1.11	0.01408
1.533	1	.01093	.01174	1	1.11	0.01408
1.710	1	.01360	.01475	1	1.11	0.01408
1.883	1	.01615	.01740	1	1.11	0.01408

It will be noted in connection with Table V., first, that the observed values agree fairly well with the calculated values, the difference

always being in the right direction; and, second, that the electromotive force due to a difference of absolute temperature represented by the ratio 1.11 is more than five times as great as that due to a corresponding difference of concentration.

Certain results obtained with the cells just described led the writer to suspect that the thermo-electromotive force in the case of silver is a certain function of the concentration of the electrolyte, as well as of the temperature. A preliminary test was made with reference to this subject. The cell used consisted of the A_1 and A_2 limbs as shown in Fig. 3. A_1 was kept at a temperature of 30°; A_2 at 0°, or thereabouts. A solution of a given concentration was placed in the cell, after which both electrodes were thoroughly agitated. The limbs of the cell were adjusted in their respective baths, and after the electromotive force had risen to a constant value, a reading was taken. The operation was then repeated with a different concentration. The thermo-electromotive force decreased with an increase of concentration of the electrolyte, as shown by Table VI., and also by Curve I., Fig. 5, which was plotted from the values of this table.

Later the test was repeated, great care being exercised in the preparation of the electrodes. A sufficiently large quantity of the precipitated silver was used to allow for a series of tests extending over that portion of Curve I., Fig. 5, which showed the most marked change of electromotive force. The precipitated silver was thoroughly washed, and dried at a temperature of about 50°. The method of procedure was as follows: Precipitated silver to the depth of one to two centimeters was placed in the bottom of each limb of the cell (A_2 and A_3, Fig. 3). A solution of $AgNO_3$ of a given concentration was then poured into the limbs A_2 and A_3 until each was about two thirds full. The contents of each limb was then thoroughly shaken, after which the conducting tubes (t) were put in place, as shown in Fig. 4. The powdered silver, which had been thoroughly incorporated with the solution in the process of shaking, quickly settled to the bottom of the tube. The two limbs were now connected by means of the siphon (Fig. 3) and the cell was then placed in position in the bath, one limb being at 25° and

the other at 0°. When the thermo-electromotive force came to a constant value a record was made.

After the test, the solution was poured out of the cell, and the precipitated silver composing the electrodes was removed. *A new portion* of the silver originally prepared was then placed in the cell, a solution of a different concentration added, and the process was repeated exactly as described above. Thus in each test practically new electrodes were employed. Three separate tests were made, each including the following concentrations: $n/80$, $n/40$, $n/20$, $n/10$. One test made with an $n/160$ solution showed very little increase in value over that of the $n/80$ solution; likewise, an $n/5$ solution gave a value only slightly below that of the $n/10$ solution. The values obtained by the three series of tests agree remarkably well with each other, as shown by Table VII. Curve II., Fig. 5, is plotted from the mean value column of this table.

TABLE VI.

Conc.	Cell A_1A_2 (Fig. 3).				Cell A_2A_3 (Fig. 3).	
	C_1/C_2	T_1/T_2	Obs. E.M.F.	Calc. E.M.F.	T_1-T_2	Obs. E.M.F.
$n/10$	1.064	30/30	0.00165	0.00170	30°	0.01253
$n/20$	1.200	30/30	507	501	30	1450
$n/40$	1.215	30/30	513	530	30	1720
$n/60$	.....	.....	.....	.....	30	1823
$n/80$	.....	.....	.....	.....	30	1850
$n/100$	.....	.....	.....	.....	30	1864

TABLE VII.

Conc.	T_1-T_2	Test 1.	Test 2.	Test 3.	Mean E.M.F.
$n/80$	25°	0.01480	0.01450	0.01440	0.01457
$n/40$	25	0.01354	0.01370	0.01330	0.01351
$n/20$	25	0.01260	0.01230	0.01252	0.01246
$n/10$	25	0.01106	0.01106	0.01140	0.01127

Curves I. and II. (Fig. 5) show a fairly good agreement. It must be kept in mind that the values represented by Curve I. are due to a difference of temperature between the two limbs of the cell of 30°; while those represented by Curve II., are due to a difference

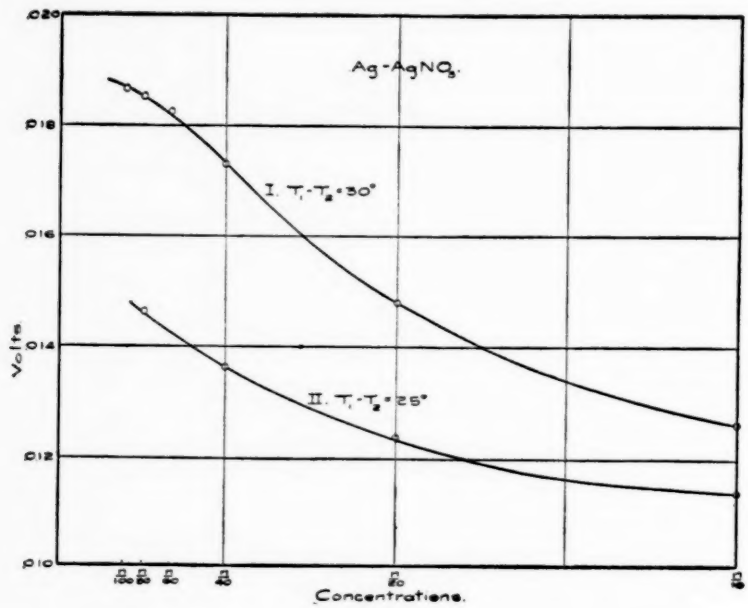

Fig. 5.

of 25°. Both indicate a maximum decrease of thermo-electromotive force between the values of one eightieth and one tenth normal.

Similar concentration curves for zinc sulphate and nickel sulphate show an *increase* of thermo-electromotive force with an increase of concentration. Such a curve for $Zn - ZnSO_4$, prepared in 1902

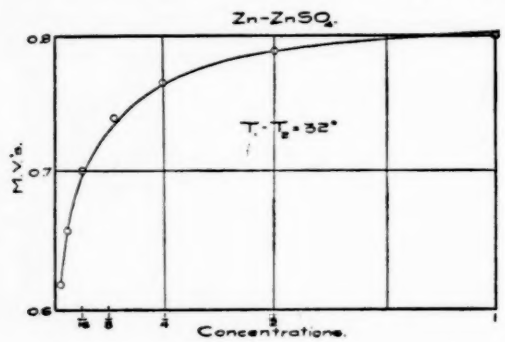

Fig. 6.

by Professor H. S. Carhart,[1] and used in the present case through his courtesy, is shown in Fig. 6. It will be noted that the curve

[1] Trans. Am. Electrochem. Soc., 2, 123, 1902.

for silver differs from that of zinc not only in direction but also in general form. This latter difference, however, is due to the portion of the respective curves chosen in plotting, and is not an intrinsic difference. The important point of the comparison lies in the difference of direction of the two curves.

Summary.

In a thermo-element of the first class, in the case of zinc, copper, cadmium and mercury, the warm electrode is the cathode. In the case of silver, on the other hand, the cold electrode is the cathode. The tests to which silver was subjected indicate that this phenomenon is not due to some peculiar property of a special electrode, since many different forms and conditions of the metal were used, and always with the same result. Cells from which the air had been thoroughly removed gave results in accord with those noted; indeed, the removal of air did not appear to affect the resulting electromotive force, either in direction or magnitude. And further, not only was the thermo-electromotive force due to a difference of 25° to 30° constant during a relatively long period of time, but also the electrodes employed gave no evidence of being changed in any respect by this difference of temperature. For example, two electrodes, prepared as described, gave, when at the same temperature, an initial reading of zero to nearly the fifth decimal place. They were then subjected to a difference of temperature of 25° for ten days, after which they were brought back to the initial condition, when both electrodes again gave practically a zero reading.

In the second place, in the case of silver, the resultant electromotive force, due to a given difference of absolute temperature, is more than five times as great as the computed osmotic pressure changes would require. Table V. shows that with a given solution, a difference of concentration represented by the ratio $C_1 : C_2$ of 1.114 gave an electromotive force of 0.00284 volt, the calculated value being 0.00291 volt; while a corresponding ratio difference of absolute temperature gave an electromotive force of 0.01408 volt, a value five times as great. When we recall that this thermo-electromotive force is directed, in the external circuit, from the cold electrode to the warm, and that no account is taken of a diminution of

ionic concentration on the cold side, due to a reduction of temperature, the result appears all the more remarkable. Theoretically, from a consideration of the increase of osmotic pressure with increase of temperature, as well as the increase of ionic concentration at the warm electrode (so far as these two factors can be considered apart from one another) we should expect to find the thermo-electromotive force of silver directed in the opposite sense; and also, we should expect to find the electromotive force due to a ratio $C_1 : C_2$ of 1.114 very nearly equal in value to the electromotive force due to a ratio $T_1 : T_2$ of 1.11. The fact that in the latter case the value is five times as great as in the former is highly suggestive that there are other factors entering into the problem besides those of osmotic pressure and solution pressure.

And finally, silver shows an anomalous change of thermo-electromotive force with change of concentration. An increase of concentration in the case of zinc, copper and cadmium gives an increase of electromotive force. In the case of silver, the reverse is true.

CONCLUSION.

The prime object of the research herein recorded was the collection and coördination of the facts bearing on the thermo-electric behavior of silver, and therefore a record of the investigation practically closes with the statements of the brief summary just given. However, while a discussion of the theories relating to the subject does not properly come within the province of the present paper, yet it will not be out of place to call attention briefly in closing to certain assumptions which suggest themselves as applicable in the explanation of the phenomena observed.

The thermo-electric behavior of silver may be explained for example, in terms of solution pressure and osmotic pressure, on the assumption that the solution pressure of the metal increases, much more rapidly with increase of temperature, than the osmotic pressure of the solution. It must be noted in this connection, however, that it will require a very large increase of solution pressure to account for the outstanding observed electromotive force. It will also be necessary to make the additional assumption that the solution pressure is a function of the concentration, as well as of the tem-

perature. And it must be noted further, that when we have made these assumptions explain the thermo-electric behavior of silver, we meet with serious difficulties in applying the same general explanation to other metals, such as zinc, or cadmium, in which cases the thermo-electromotive force is directed in the opposite sense.

Again, a provisional explanation may be given on the assumption that certain thermo-chemical changes occur in the electrolyte, affecting the degree of dissociation of the salt in solution by the formation of new compounds, as for example, the products of hydrolysis.

In the third place, the phenomena observed with respect to silver may be due to the surface conditions of the electrodes used. For example, if the electrode were covered with a film of oxide, which is assumed to undergo a change more readily on the warm side of the cell than on the cold, there would undoubtedly be established conditions favorable for the production of an electromotive force.

And, to conclude, the peculiar thermo-electric behavior of silver may be explained by applying the assumptions embodied in the Carhart thermo-electric theory of concentration cells — namely, that there is a thermo-electromotive force between a metal and its salt analogous to that between two different metals, and that this thermo-electromotive force is a function of both the temperature and the concentration ; and further, that the direction of the thermo-electromotive force, from the metal to the solution or vice versa, depends upon the nature of the metal composing the electrode. The assumptions in this case take no account of forces operating to produce such an electromotive force other than the energy changes which are due to differences of temperature, and which operate in accordance with the laws of thermo-dynamics. These assumptions give an explanation in accordance with the facts ; they offer, however, no clue to the mechanism by which the thermo-electromotive force is brought about.

Whatever may prove to be the true explanation of the thermo-electric behavior of silver, certain it is that much remains to be done before very definite statements can be made with reference to this subject or to the more general problem of the relation of heat to electromotive force.

It is planned to continue the present research, dealing with the subject of the thermo-electric behavior of silver over a greater range of temperature than that touched upon in the present case, and also to investigate further the relation of oxidation to thermo-electromotive force.

In conclusion the writer wishes to acknowledge his indebtedness for the loan of a number of important pieces of apparatus by the department of physical chemistry of the University of Michigan, in which department the major portion of the work was done; and to express his appreciation of the interest shown in the work by Prof. H. S. Carhart, of the department of physics, under whose direction the investigation was carried on.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
March 6, 1906.

INFRA-RED ABSORPTION AND REFLECTION SPECTRA.[1]

By Wm. W. Coblentz.

Introduction.

MANY chemical compounds contain both oxygen and hydrogen, which, on applying heat, pass off in the form of water. That the water is not united so tenaciously as the other constituents is evident from the fact that in many instances it can be more easily removed; many salts give up their water if exposed to dry air at ordinary temperature. From the circumstance that many of these compounds are crystalline the water is said to be present as *water of crystallization.* The manner in which the water exists in the crystal is not understood. By some it is considered a part of the chemical molecule; by others it is thought that the molecules of water exist in their entirety among the molecules which constitute the crystal. It is characteristic of water of crystallization that it is expelled at a temperature far below red heat, and frequently below 100° C. Another characteristic of minerals containing water of crystallization is their property of reabsorbing water after it has been removed. Copper sulphate is an excellent example; on applying heat, the blue crystal becomes a crumbling white mass, which, if permitted to stand in dry air absorbs water and resumes its blue color and crystalline structure.

On the other hand, the water which is given off only at a red or even a white heat can scarcely be present in the compound in the same manner as the water of crystallization, and is distinguished as *water of constitution.* In this case the water is not supposed to exist as such in the mineral, but to result from the union of oxygen and hydrogen or from the hydroxyl groups contained in the compound.

[1] Extracts from a memoir submitted to the National Bureau of Standards for publication.

Of course there are minerals which contain water in both these forms. In copper sulphate, $CuSO_4 + 5H_2O$, four molecules of water are given off at 100° and the fifth at 200° so that the latter is possibly combined in some manner different from the former. In epsomite, $MgSO_4 + 7H_2O$, six molecules of water are given off at 132° while the seventh is held more tenaciously and is not given off until heated to 210°.

However, in cases like these, where successive portions of water are given off at different temperatures, it is difficult to draw a distinction between water of crystallization and water of constitution. In the minerals just quoted, however, it has been found that the heat of hydration of the last molecule of water is different from that of the molecules of water which pass off at a lower temperature, which confirms the belief of a difference in the bonding in the two cases.

As a whole, the question of the association of the atoms of oxygen and hydrogen in certain compounds is far from settled, while the difficulties involved in its investigation are very great. The existing data bearing upon the subject is practically *nil.*

PRESENT METHOD OF INVESTIGATION.

In a preliminary paper bearing upon the question of water of crystallization[1] the writer described the infra-red absorption spectra of two numerals, selenite, $CuSO_4 + 2H_2O$, and brucite, $Mg(OH)_2$, in which the atoms of oxygen and of hydrogen are thought to be combined in a different manner. It was the application of the results of previous work in which it was abundantly proven that certain groups of atoms have characteristic absorption bands. Hence, if the oxygen and hydrogen, which enter into the composition of certain minerals, are bonded as they are in a molecule of water then one would expect to find the absorption spectra of such minerals to be a composite of the bands of ordinary water and of the bands caused by the other constituents.

The only previous investigation bearing on this subject, from the standpoint of infra-red absorption spectra is that of Königsberger,[2]

[1] PHYSICAL REVIEW, 20, p. 252, 1905.

[2] Königsberger, Ann. der Phys., 61, p. 703, 1897.

who studied the pleochroism of several minerals including selenite. Unfortunately his plate of selenite was too thick, so that no energy was transmitted beyond 2.5 μ. He calls attention to the fact that a small absorption band at 1.5 μ coincides with that of water, from which it would appear that in selenite the absorption of the water of crystallization does not appear to be different from that of ordinary water.

Thinking that it would be fairer to select the *large* water bands at 3.0, 4.75 and 6 μ as a criterion, the writer (loc. cit.) examined *thin* sections of several minerals and found as anticipated that minerals containing water of crystallization have large absorption bands coinciding with those of ordinary water. The selection of selinite, $CaSO_4 + 2H_2O$, and brucite, $Mg(OH)_2$, as types of water of crystallization and of constitution was a fortunate one, for two reasons. (1) The selenite curve showed all the absorption bands of water in their proper positions and intensities, except the 4.65 μ band which is shifted and too deep for the thickness of water contained in the plate under examination. The fact that the band is shifted caused me to suspect that it may be complex, and, from the fact that it lies in the region where the NCS-radical and certain sulphur compounds have a strong absorption band, that it may be due to the SO_4-radical, a surmise that since then has been unexpectedly verified. (2) Although the brucite curve did not contain the water bands, thus showing the difference between water of constitution and of crystallization, it contradicted my previous work[1] in which it was shown that the OH-radical in the alcohols has an absorption band at 2.95 μ. From the brucite curve the conclusion was drawn that the OH-radical is inactive. Since then I have studied the chemical side of the question more thoroughly from which it appears that there is no marked difference[2] in the activity of the OH-radical in the hydroxide studied, and hence that the brucite curve should have a band at 3.0 μ instead of the one shifted to 2.5 μ. In other words, the present research, which is in part the outcome of the

[1] Investigations of Infra-red Spectra, Washington, 1905. PHYS. REV., Vol. 22, 1905.

[2] From the chemical standpoint, however, the OH in alcohol and in H_2SO_4 is more active, since it is replacable by a metal (more acid) than the OH in brucite $MgO(OH)_2$, which is not replacable (more basic).

aforesaid discrepancies, has to a very unexpected degree furnished us with an abundance of new proof that certain groups of atoms have definite absorption bands, which really means that these groups of atoms, or "ions" enter into the various compounds in a similar manner.

To sum up, in the present investigation the criterion for distinguishing water of crystallization from water of constitution, is the presence of absorption bands at 1.5, 2, 3, 4.75 and 6 μ, which is the location of the absorption bands of ordinary water. If there are no other absorption bands nearby then the intensity of these bands should be somewhat like that of ordinary water, viz.: the bands at 1.5, 2, and 4.75 μ are weak, while the bands at 3 and 6 μ are very strong.

A hydroxyl group will cause an absorption band at 3 μ. Silicates may have a small band shifting from 2.9 to 3.1 μ, but since it is weak, there is no danger of confusing it with the strong water band in the same region.

PLEOCHROISM.

Since the present research involves the examination of minerals which are not isotropic, the question presents itself whether it would be better to examine them in natural or polarized light. In the former case we obtain *all* the absorption bands, irrespective of the direction of transmission, but their observed intensities will not necessarily be real. In the latter case where the intensity of the transmitted energy depends upon the direction of vibration of the polarized rays with respect to the axes of the crystal (pleochroism) the observed intensities will be real, the number and position of the absorption bands will depend upon the direction of observation, but the accuracy is less the farther one penetrates the infra-red, due to the loss in the polarizing the source of energy.

By these statements it is not intended to give the impression that pleochroism is not worth considering. The work of Merritt[1] and of Königsberger[2] is especially valuable in demonstrating that absorption is dependent upon the direction of vibration of the incident energy. The visible spectrum is so narrow that it is difficult to

[1] Merritt, PHYS. REV., 2, p. 424, 1894.
[2] Königsberger, Ann. der Phys., 61, p. 687, 1897.

separate the absorption bands, while, on the other hand, the infra-red is a vast and almost unexplored region, and it is here that one would expect to resolve wide absorption bands such as exist in the visible spectrum. The curves of Merritt and of Kōnigsberger show this, especially the calcite curves, which are entirely independent for the ordinary and extraordinary rays. Nevertheless, in looking over the previous work it seemed to the writer that in the present state of our knowledge of absorption a greater advance would be made by simply mapping the spectra of a great many minerals for energy transmitted through them in its natural mode of vibration. The results have been most gratifying. If we had been content with the examination of a few, easily obtainable, large-sized crystals like colemanite, for pleochroism, the results would have been quite different.

The maxima of the absorption of water are constant in position for the amorphous and the crystalline minerals studied, which would indicate that in this case the transmission is not affected by the direction of vibration.

The desirability of examining many minerals is illustrated in the appended curves in which it will be seen that frequently in one region of the spectrum the water bands are obliterated by an increase in the general absorption or by an adjacent absorption band, while in another part of the spectrum the water bands are very distinct.

Apparatus and Methods.

In the present investigation a mirror spectrometer, a rock slat prism and a Nichols' radiometer were used. Except for certain improvements, the details in mounting and adjusting the different parts have been described elsewhere[1] and it will be sufficient to add that the spectrometer mirrors were 10 cm. in diameter and 50 cm. in focal length, and that the rock salt prism was an unusually fine one, having a refracting angle of 59° 59′ 36″ and faces 9 × 9 cm. area. The spectrometer slits were 0.3 mm. wide, or about 2′ of arc. The time required for the radiometer to reach a maximum deflection was about 20 seconds. The different portions of the

[1] Phys. Rev., Vols. 16 and 17, 1903. Investigations of Infra-red Spectra, Washington, 1905.

spectrum were projected upon the radiometer slit by using the Wadsworth[1] mirror-prism method and rotating the prism table. Although one doubles the error in making spectrometer settings, the method was the most convenient one in the present work. The "heater" of a 110 Nernst lamp, on an 80-volt storage battery circuit was used as a source of energy. The sections were mounted in the usual manner, upon a wooden carrier which moved in vertical ways between the source of energy and the collimeter slit.

To protect the prism from moisture a small crystallizing dish of P_2O_5 was placed over it, and when not in use, a large crystallizing dish was inverted over the prism and drying material. The edge of the large dish was ground to fit the prism table, and prevented the entrance of moisture.

PREPARATION OF THE MINERAL SECTIONS.

Whenever possible the crystals were split parallel to a cleavage plane, since many crystals would break in grinding. The remaining ones were ground thin in the ordinary manner. To accomplish this they were mounted upon glass plates by means of pitch, having a low melting point so as to avoid disturbing the water of crystallization which is expelled from some minerals at a low temperature. The sections were cleaned in chloroform and mounted upon heavy cardboard having rectangular holes about 4 × 10 mm. cut into them. That the crystals were not affected by grinding and the cement was proven in a number of cases where cleavage sections of the same mineral were examined. The sections were entirely free except at the ends which rested upon the cardboard, which was then mounted upon the holder which moved in vertical ways before the spectrometer slit.

In the description of the different minerals, the direction of cutting the sections is parallel ($\| a$) to some crystallographic axis. In many crystals there is usually a perfect cleavage parallel to one of the crpstallographic axes, which fact was taken advantage of in preparing the sections. The cleaving was done by means of a small knife-blade struck with a light piece of metal, for example, a file.

In the present research the examination of the sections after being prepared was overshadowed by the difficulty in obtaining specimens

[1] Wadsworth, Phil. Mag. (5), 38, p. 346, 1894.

of sufficient size and in grinding them thin enough. In my previous work it was found that as a general rule the compounds examined increase in their general absorption beyond 5 μ, so that the (liquid) films had to be reduced to 0.01 mm. In the present work it was impossible to reduce the thickness to much less than 0.1 mm. with the consequent result that many sections became opaque beyond 5 μ.

The minerals were obtained from various dealers and from the U. S. National Museum. They were selected according to composition. Of the total number thus selected only about 40 per cent. were obtainable and these were oftentimes the least desirable to illustrate the points in question. The expense involved is no small item, and I am very grateful to the Director for his generosity in meeting that question.

Scope of Present Investigation.

The principal object in this research was to gain information in regard to the molecular structure of minerals containing oxygen and hydrogen. To this end minerals were selected containing these constituents. Previous work has shown that in organic compounds certain radicals have characteristic absorption bands. One would therefore naturally expect to find similar relations in inorganic compounds, where more important radicals are to be found. Hence, the list was extended, so as to contain a series of minerals having the radicals CO_2, PO_4, SO_4 and OH. The results obtained serve the purpose very well for demonstrating the rashness to attempt to establish "laws" from present data for future investigators to refute, just as is being done at present in more thoroughly explored fields, such as for example the absorption of solids in solution.

In the study of the carbon compounds in inorganic chemistry, their constitution has been established by the replacement of certain constituents by organic radicals, by the preparation of a series of derivatives, by vapor density determinations or by studying their physical properties in solution. Mineralogy is essentially the chemistry of silicon compounds, to which, as yet, it has not been possible to apply any of the above methods, so that the constitution of many minerals has been derived from analogies with other compounds which are better understood. Hence, in an investigation

like the present it is not surprising to find exceptions to the tentative rules for classifying these minerals.

The transmission curves are given without correction for reflection on the surfaces. In most cases, as will be noticed from the reflection curves, the correction is negligible. One case, viz., stibnite, Sb_2S_3, such a correction is worthy of notice. The transmission shows a uniform value of 45 per cent. To the writer this seemed a very transparent substance until the greater surprise of a uniform reflecting power of about 43 per cent. was observed, which indicates that after correcting for reflection this mineral (for the thickness examined) is practically transparent.

ABSORPTION SPECTRA OF DIFFERENT MINERALS.

Group I., Minerals Containing Water of Crystallization.

Under this heading are to be found all the minerals studied which are generally thought to contain water of crystallization. First of

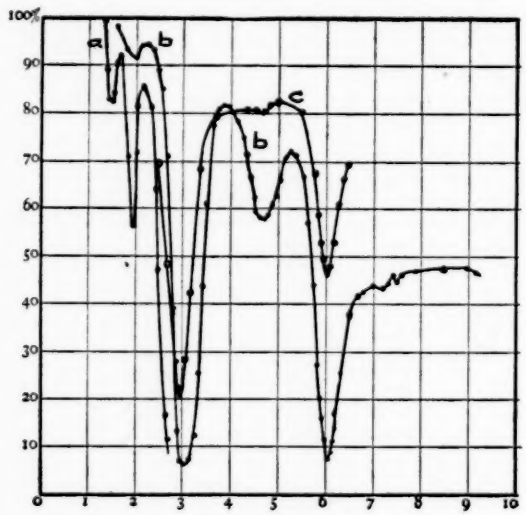

Fig. 1. Water.

all it will be necessary to consider the absorption spectrum of water which has been studied by Julius,[1] Paschen,[2] Aschkinass[3] and

[1] Julius, Verhandl. Königl. Akad. Amsterdam, Deel I., No. 1, 1892.

[2] Paschen, Ann. der Phys. (3), 53, p. 334, 1894.

[3] Aschkinass, Ann. der Phys. (3), 55, p. 406, 1895.

others. All observers agree in their location of large absorption bands at the approximate wave-lengths 1.5, 3, 4.75 and 6 μ.

All have found water extremely opaque to infra-red radiation, so that the film had to be reduced to a few thousandths of a millimeter in order to be able to study it at all. In Fig. 1 are given the absorption curves (a and b) of water as found by Aschkinass. His values of the maxima are slightly greater than those found by others, but this is simply due to a fault in his calibration. The curves for the different thicknesses ($a = .05$, $b = .01$ mm.) illustrate very well what we are to expect in the case of minerals containing several molecules of crystal water. For a very much thinner film

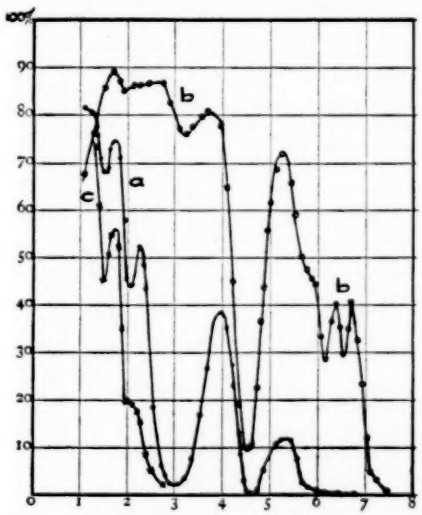

Fig. 2. a = Selenite, $t = 0.648$ mm., b = Anhydrite, $t = 0.656$ mm., c = Selenite, $t = 2.57$ mm.

(curve $c = .001$ mm.) examined by the writer[1] the absorption band at 4.75 μ has entirely disappeared.

SELENITE, $CuSO_4 + 2H_2O$.

ANHYDRITE, $CaSO_4$.

(Figs. 2 and 3; selenite monoclinic, cleavage $\| b$, $t = .648$ mm. Anhydrite, orthorhombic cleavage piece $\| c$, $t = .656$ mm., from Stassfurt, Germany.)

Of all the minerals studied containing water of crystallization these two are the most conspicuous for demonstrating the effect of

[1] PHYS. REV., 20, p. 257, 1905.

the presence of H_2O. It would have been highly desirable to procure more minerals which occur in the hydrous and anhydrous state, but none were obtainable. The artificially dehydrated minerals, such as copper sulphate, were too opaque for examination after expelling all the water. The only exception is selenite, the various curves of which will now be considered. The anhydrite curve, *b*, is to be noticed first, from which it will be observed that there are small bands at 1.9, 3.2, 5.7, 6.15 and 6.55 μ and an enormous band at 4.55 μ, which will be shown later to be due to the SO_4 ion.

Turning to the selenite curve, *a*, Fig. 2, it will be noticed that it is less transparent for the same thickness, 0.65 mm., and that in its general trend it is similar to the curve for water. All of its absorption bands coincide with water, with the exception of the 4.75 μ, as was found on examining the anhydrite. The band 3 μ is widened by the presence of the anhydrite band at 3.2 μ. The curve *c* for a thickness of 2.57 mm. is due to Königsberger (loc. cit.).

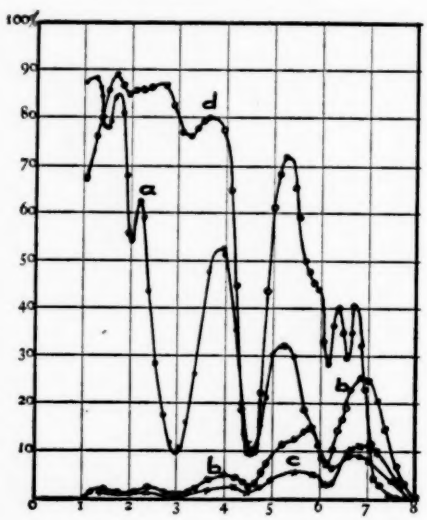

Fig. 3. *a*, *b*, *c*, = Selenite, $t = 0.204$ mm. *d* = Anhydrite, $t = 0.656$ mm.

In Fig. 3 is illustrated the effect of dehydrating the selenite. This was accomplished with difficulty on account of the warping and shrinking of the plate, which necessitated the dismounting of the specimen for each heating. It was found necessary to clamp the

specimen between two metal plates in order to prevent it from warping and breaking. Curve *a* gives the clear piece having a thickness of 0.204 mm. Curve *b* shows the transmission after partial dehydration. It is of considerable interest in showing the permanence of the 4.55 μ band. Beyond 6 μ the transparency increases and becomes 1.5 times as great as selenite at 6.9 μ. The dehydrated section, which is an opaque white mass, was then moistened with water and allowed to stand over night to dry and set, just as in the case of plaster of paris. The result is shown in curve *c*, where the transparency at 6.9 μ has decreased to almost the original value found for the transparent crystal. It will of course be understood that the great opacity up to 5 μ for the dehydrated section is

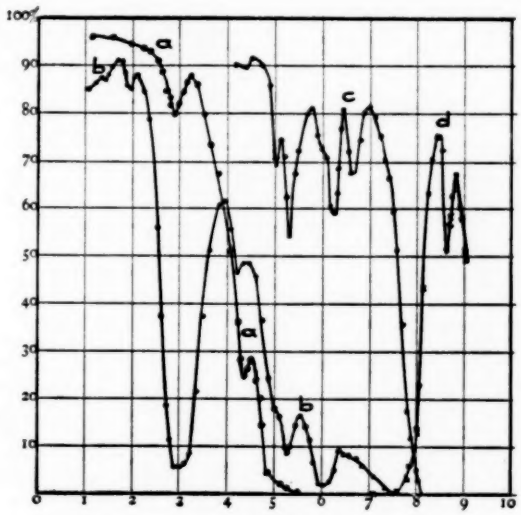

Fig. 4. *a*, *c*, *d*, = Quartz ; *b* = Opal.

due to the lack of homogeneity introduced in expelling the water, which has the well known property of scattering the radiation of short wave-lengths. At 7 μ the increase in absorption due to the presence of water cannot be doubted.

QUARTZ, $SiO_2 = SiO_2$.
OPAL, $SiO_2 + xH_2O$.

(Quartz cut axis. $t = 1.30$ mm. Opal, massive, transparent. $t = 0.12$ mm.; Fig. 4.)

The specimen of quartz examined was made for polariscopic work and was perfectly clear. Its transmission curve, *a*, Fig. 4, shows small bands at 2.9 μ and 4.35 μ. Curve *c*, which shows a series of bands at 5.02, 5.3, 6, 6.26 and 6.65 μ, is due to Nichols[1] who used a section 0.018 mm. thick. Unfortunately his curve begins in the slight band at 4.35 μ so that there is no check upon its accuracy of location.

Königsberger[2] examined smoky quartz and found bands at 3.05 and 4.05 μ. Merritt[3] using polarized light found bands at 3 and 3.6 μ for the extraordinary ray, and bands at 2.9, 3.75 and 4.1 μ for the ordinary ray.

For amethyst, which is violet quartz, of which the color has been attributed to manganese, Königsberger found an absorption band at 3.1 μ. As a whole different observers agree in locating a small band near 3 μ which will not interfere in considering water of crystallization.

Opal is quartz containing variable proportions of water, from 5 to 30 per cent. It shows no traces of crystallization. Neither is it considered a solid solution, for the water contained is not a function of the vapor pressure. The transmission curve of opal has the general outline of the curve for water and contains the bands of water at 1.5, 2, 3 and 6 μ, as well as the silicon bands at 4.2 and 5 μ. The 3 and 6 μ bands are the composite of the water and silicon bands in those regions.

HEULANDITE, $H_4CaAl_2Si_6O_{18} + 3H_2O$.

(Section ground $\parallel b$. $t = 0.20$ and 0.22 mm., semitransparent. Fig. 5).

Heulandite belongs to a class of minerals called zeolites[4] which are hydrated silicates of alumina, alkalies and generally lime. To this class belong heulandite, stilbite, analcite, natrolite and scolecite, which are included in the present research.

In these minerals the water of crystallization is very loosely held. It is impossible to distinguish between water of constitution and water of crystallization. The water continues to be gradually

[1] Nichols, PHYS. REV., 4, p. 297, 1896.
[2] Königsberger, Ann. der Phys. (3), 61, p. 687, 1897.
[3] Merritt, Ann. der Phys. (3), 55, p. 49, 1895.
[4] Miers, Mineralogy, p. 483.

expelled as the temperature is raised and may be replaced by other substances such as NH_3H_2S or C_2H_5OH. The dehydrated crystals absorb definite quantities of these substances, as a sponge absorbs water, the process being accompanied by the evolution of heat.

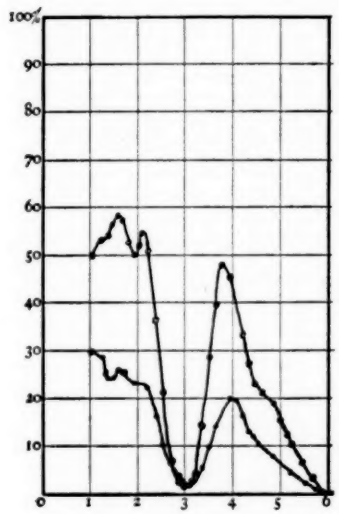

Fig. 5. Heulandite.

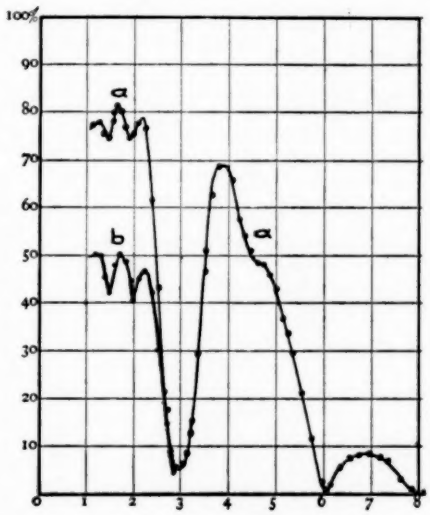

Fig. 6. Stilbite (a) and Potassium Alum.

Since the per cent. of water present varies continuously with the vapor pressure it is generally concluded that the water of the zeolites is not analogous to the water of crystallization of most hydrated salts, but resembles more nearly the intermixture which occurs in solid solutions.

In Fig. 5 two curves of heulandite are given. The sections were about the same thickness and the great difference in transparency is due to the fact that the crystals were of different homogeneity and transparency. The curves show the presence of the water bands at 1.5, 2, 3 and 4.75 μ beyond which point the opacity becomes too great for further exploration.

The crystals obtainable were small, so that the section was not quite long enough to cover the whole slit.

STILBITE, $CaAl_2Si_6O_{16} + 6H_2O$.

(Transparent section cut $\perp$ to optic axis. $t = 0.11$; curve a, Fig. 6.)

The stilbite curve is to be noticed for its great transparency with all the water bands superposed. There do not appear to be any important bands belonging to the mineral itself.

POTASSIUM ALUM, $K_2SO_4Al_2(SO_4)_3 + 24H_2O$.

(Cut ⊥ axis. $t = .085$ mm., transparent; curve *b*, Fig. 6.)

The exploration of the spectrum extends only to 3 μ. The water bands at 1.5 and 2 μ are present. With 24 molecules of water and SO_4 bands at 4.55 μ, to be mentioned later, it would not be possible to penetrate beyond 3 μ, unless a thinner section could be made.

NATROLITE, $Na_2Al_2Si_3O_3O_{10} + 2H_2O$.

(Orthorhombic section ground ‖ *m*, subtranslucent. $t = 0.11$ mm.; curve *a*, Fig. 7.)

The specimen from which this section was cut was a tuft of acicular crystals. The section was made from the more massive part, and was almost opaque for the thickness used. The curve *a*, in Fig. 8, shows the water bands in their usual positions and proper intensities.

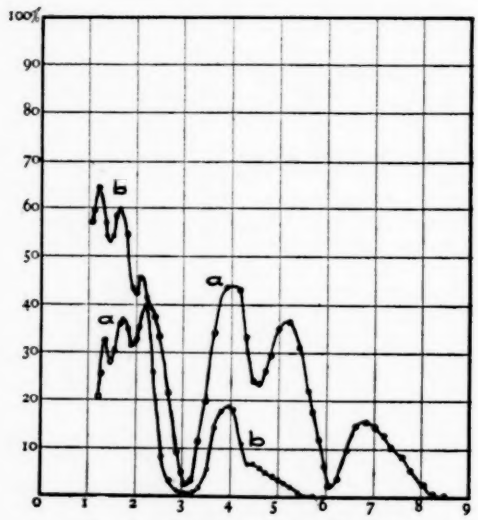

Fig. 7. Natrolite (*a*) and Scolecite.

SCOLECITE, $CaAl_2Si_3O_{10} + 3H_2O$.

(Monoclinic, section split ‖ *m*, perfectly transparent. $t = 0.565$ mm.; curve *b*, Fig. 7.)

This mineral differs from the preceding in being a lime zeolite, and having one more molecule of water. Its greater homogeneity makes it more transparent in the region of the short wave-lengths. It has the general outline and the absorption bands of water up to 5 μ where it is completely opaque. The 3 μ band is evidently complex. Professor S. L. Penfield kindly presented this specimen.

CALCIUM CHLORIDE, $CaCl_2 + 6H_2O$.

(Film melted between rock salt. $t = 0.1$ mm., Fig. 8.)

This compound comes in large hexagonal crystals. A specimen was melted between two plates of rock salt, and stood over P_2O_5 for several days, until the edges became white from dehydration. The substance recrystallized in the meantime, and when examined showed the water bands in their usual position and intensities, except the 3 μ band which is shifted to 3.2 μ.

POTASSIUM FERROCYANIDE, $K_4Fe(CN)_6 + 3H_2O$.

(Section split $\parallel c$, transparent. $t = 0.3$ mm.; curve *b*, Fig. 8.)

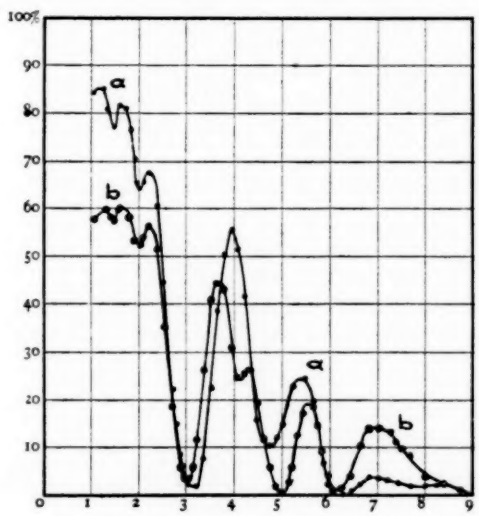

Fig. 8.

The water is so easily expelled from this mineral that the heater had to be used on 70 volts. The transmission curves show the water bands at 1.5, 2 and 3 μ, while the next two bands are shifted

to 5 and 6.2 μ respectively. Porter[1] by means of "reststrahlen" located a band at 4.84 μ.

MELLITE, $Al_2C_{12}O_{12} + 18H_2O$ (Fig. 9).

This mineral occurs as waxy crystals of variable transparency in European coal measures. It was selected on account of its carbon, and also because of the large number of molecules of water, which is expelled at a low temperature.

In Fig. 9 curve *a* is given the transmission curve of a mineral from Steeg & Reuter, purporting to be mellite or "honeystone,"

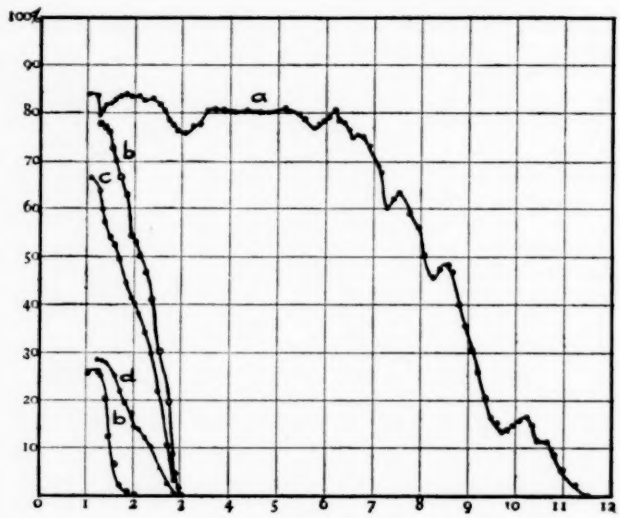

Fig. 9.

$t = .125$ mm. It was the most flagrant exception of the rule that minerals having water of crystallization are very opaque and have absorption bands in common with water. Evidently this needed further investigation; and this was done with minerals purchased from various dealers, care being taken to obtain them from different localities. Curves *b* and *c* give the transmission for transparent yellow crystals, $t = 0.7$ and 0.15 mm., respectively, which came from Arten, Thuringia. Curve *d* is the transmission for a grayish white transluscent crystal, ground to 0.12 mm. in thickness, from Mallonka, Austria. Curve *e* is for a white transparent crystal, 0.06

[1] Porter, Ap. Jr., **22**, p. 229, 1906.

mm. in thickness, from Tula, Russia. In all these curves it will be noticed there is no energy transmitted beyond 3 μ, while from the very nature of the transmission curves the 1.5 band is invisible, while the 2 μ band is almost obliterated. As a whole the theory that in crystal water the bonding is the same as in ordinary water has also been confirmed with mellite. A letter of inquiry to Steeg & Reuter in regard to the sample sent us revealed the fact that cassiterite, SnO_2, was accidentally substituted for mellite. The fact that it was possible to detect the error would indicate that the method of analysis is trustworthy, and in that respect it is fortunate that the substitution occurred.

About twenty other substances were examined which contain water of crystallization and they all show the bands of ordinary water. The list includes a number of sugars, nearly all of which contain water of crystallization. One of these sugars, *d*-fructose, $C_6H_{12}O_6$, does *not* show water bands, as was to be expected. Cane sugar, $C_{12}H_{22}O_{11}$, whether in a melted condition or a crystal, "rock candy," *shows water bands.* An analysis showed that the water content was about 0.05 per cent., which is too small an amount to account for the bands. Now, it has never before been suspected that cane sugar has water of crystallization and the present disagreement with the results of chemists who have made a life-long study of sugars in general must be considered with caution. A comparison with lactose, maltose and dextrose would indicate the presence of a molecule of water in crystallization.

Sugars are rich in OH groups, which with the CH_3 will confuse matters at 3 to 3.5 μ, so that the effect of water must be based upon the small bands at 1.5 and 4.75 μ. As a whole, the question is obviously in an unsettled state, with the present data indicating the presence of a molecule of water of crystallization in cane sugar which has heretofore been considered to be composed entirely of water of constitution.

Group II., Minerals Containing Water of Constitution.

The first part of this group contains minerals in which the oxygen and hydrogen are present in the form of the univalent hydroxyl radical, OH, and which are known as hydroxides. The hydroxides

when heated also yield water, but it is a characteristic that they must be strongly heated before they are decomposed. From previous work, already noticed we would expect an absorption band at 3 μ for hydroxides.

Manganite, MnO(OH).

(Orthorhombic, ground $\parallel$ *m* opaque, $t = 0.08$ mm., Fig. 10.)

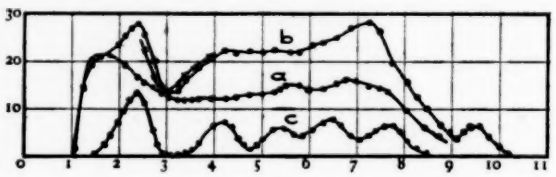

Fig. 10.

As will be noticed in curve *a* of Fig. 10, manganite has no sharp bands throughout the whole region to 9 μ. There is a slight indication of a band at 3 μ, and another at 6.2 μ.

Gothite, FeO(OH).

(Section ground $\parallel$ *b*, $t = 0.15$ mm., curve *b*, Fig. 10.)

The appearance of this mineral is opaque, black metallic luster, and as a whole would not impress one as being quite transparent to 9 μ. It transmits about 20 per cent. of energy throughout this whole region, which is in marked contrast with the almost complete opacity of iron. The 3 μ band is well-marked while a second one occurs at 9 μ. This specimen was kindly presented by Professor S. L. Penfield.

Bauxite, $Al_2O(OH)_4$.

(Chocolate-brown color. $t = 0.11$ mm., curve *c*, Fig. 10.)

In this mineral the 3 μ band is wide and complex. There are other bands at 4.7, 5.8 and 7 μ.

Turquoise, $AlPO_4$. $Al(OH)_3 + H_2O$.

(Massive light-green. Subtransparent in section of 0.1 mm., curve *a*, Fig. 27).

This mineral is supposed to contain a molecule of water, although Miers writes the formula without it. The OH groups will cause a band at 3 μ and in general the substance is very opaque so that it is difficult to decide that question. The region at 3 μ is complex

with the maximum at 3.3. There are other bands at 5.1, 5.3, 5.6, 6.3 and 7.6 μ, all of which are small. There seem to be no bands belonging to PO_4.

LAZULITE, $(Mg.Fe)Al_2(OH)_2(PO_4)_2$.

(Massive blue by transmission. $t = 0.19$ mm., curve *b*, Fig. 27.)

The 3 μ band is prominent, while a new band appears at 4.3 μ.

HYDRARGILLITE, $Al(OH)_3$.

(Stalactitic mass, $t = .02$ mm., subtransparent, curve *a*, Fig. 11.)

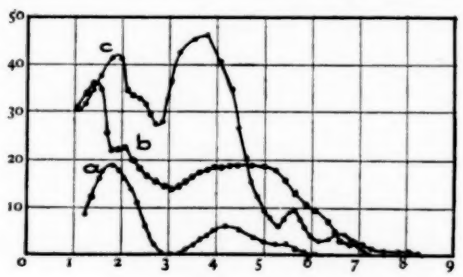

Fig. 11.

The section obtainable was only about 6 mm. long, which did not cover the entire slit, hence the opacity is not quite so great as it appears. There is only one large band, at 3 μ, which is no doubt due to the OH radicals.

DIASPORE, AlO(OH).

(Cleavage piece $\parallel b$. $t = 0.18$, curve *b*, Fig. 11.)

The specimen was transparent with a few particles that were translucent. The specimen came from Professor Penfield. The band at 3 μ is wider, not so well defined as in the preceding. There are smaller absorption bands at 1.9, 5.8 and 6.7 μ.

DATOLITE, $Ca(BOH)SiO_4$.

(Section ground to 0.23 mm., curve *c*, Fig. 11.)

In the curve the OH band at 3 μ is shifted to 2.8 μ. The other bands present are at 2.3, 5.3 and 6.3 μ. Although the specimen was full of cracks it is rather transparent for a boro-silicate.

AZURITE, $2CuCO_3.Cu(OH)_2$.

(Translucent section $\parallel c$. $t = 0.35$ mm. thick, curve *c*, Fig. 12.)

The section was ground from a group of crystals all of which were apparently $\parallel c$. There are absorption bands at 2.5, 3.05, 3.58

and 4.05 μ and complete opacity beyond 5.5μ. The 3.05 μ band is shifted slightly from the position common to substances containing OH groups.

BRUCITE, $Mg(OH)_2$.

(From Woods' Mine, Lancaster Co., Pa. Foliated, massive, lamina $\parallel$ c. $t = .05$ and $t = 0.19$ mm., Fig. 12.)

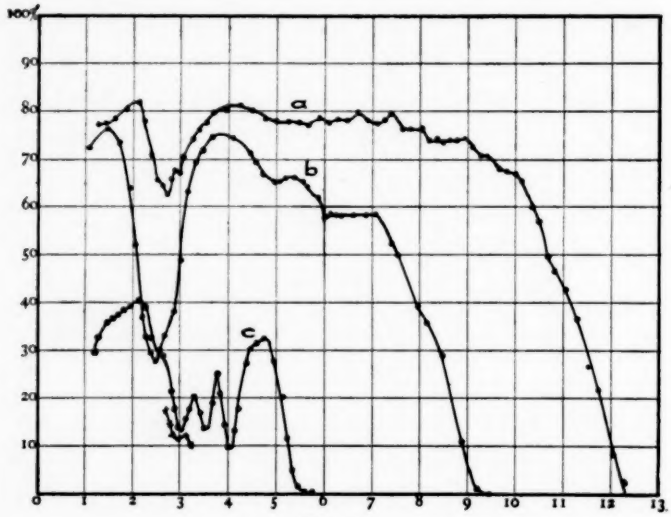

Fig. 12.

As mentioned elsewhere, the fact that brucite did not show an absorption band at 3 μ, which is the maximum of the hydroxyl group in a series of organic compounds previously studied, made a reëxamination highly desirable. Of course, as will be noticed in curve *b*, by straining matters one might have concluded that the band at 2.5 μ, which evidently is complex, contains the 3 μ band. In the present examination the cleavage section was perfectly transparent and much thinner than the previous one. Furthermore the dispersion is greater, so that as a whole this large band is resolved into three components with maxima at 2.5, 2.7 and 3 μ. Beyond this region these are no marked bands, while beyond 12 μ there is complete opacity. The curves show depressions at 5, 7, 7.7, 8.2, 9.7 and 10.8 μ, but as a whole the curve is conspicuous for the complete absence of sharp absorption bands, except at 2.7 μ, which is similar to glass and the micas.

PORTLAND CEMENT.

($t = 0.17$ mm.)

The specimen examined was ground thin from a piece made for tensile strength tests. It is known as the "Atlas Brand" and in making it was mixed with 21 per cent. of water. The chemical constitution of Portland cement is unknown. According to le Chatlier[1] the action of water causes the formation of a hydrous silicate $(SiO_2.CaO.).5H_2O$ and a hydrous aluminate $Al_2O_3 4CaO. 12H_2O$.

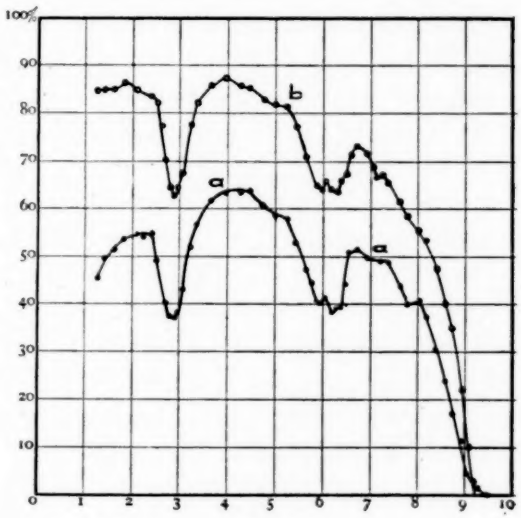

Fig. 13.

From the present curve it will be noticed that the substance is very opaque, with a large absorption band at 3 μ, which would seem to indicate hydroxyl groups. From the curves of mellite and alum it appears that Portland cement is too transparent to contain the number of molecules of water indicated by le Chatlier.

CHLORITOID, $H2(Mg.Fe.)Al_2SiO_7$.

(Variety masonite, cleavage piece $\parallel c$, transmits blue-green. $t = 0.25$ mm.)

This mineral is very opaque to infra-red radiation. There are several small absorption bands, viz.: at 2.3, 2.6, 3.3, 5.6 and 6.3 μ.

[1] Le Chatlier, Annales des Mines, February, 1888.

As in the preceding, the point of interest is the absence of bands at 1.5 and 3 μ.

CLINOCHLORE, $H_8Mg_5Al_2Si_3O_{18}$.

PENINITE, $H_8(Mg, Fe)_5Al_2Si_3O_{18}$.

(Clinochlore, $t = .08$ mm. Peninite, curve b, $t = .04$ mm., Fig. 13.)

These two minerals belong to the chlorite group, which is related to the micas, to be noticed presently. These minerals contain about 12 per cent. of water, which is given off at a high temperature.

Their transmission curves are usually similar to those of the micas. There are absorption bands at 2.9, 5.9, 6.3, 7.1 and 7.8 μ. The frequently recurring bands at 2.9 and 5.9 μ with the metallic reflection band at 8.5 and 9.02 μ reminds one of a harmonic series. It may be that these bands belong to a slowly converging spectral series, if not a harmonic series; for the first band oscillates between the values 2.8 and 2.95 μ, while the next band shifts from 5.6 to 5.9 μ, as will be noticed in the micas. As already mentioned the constitution of many minerals is still doubtful. Clinochlore is one of these. From analyses made by Clarke and Schneider[1] it was inferred that the hydroxyl groups MgOH and $Al(OH)_2$ are present. In the present examination there is no indication of a band at 3 μ, which is a characteristic of the OH radical.

TOURMALINE, $H_6Na_2Fe_4B_6Al_3Si_{12}O_{63}$.

(Cut $\parallel$ optic axis.)

These curves are due to Merritt (loc. cit.) and show the variation in transmission for the ordinary ray (plotted ——) for the extraordinary ray (——) and for the unpolarized light. The important absorption bands are at 1.28 and 2.82 μ. The latter is to be noticed in considering the effect of SiO_2, SiO_3 and SiO_4 groups.

MICAS { *Muscovite*, $H_2KAl_3(SiO_4)_3$. *Biotite*, $(H, K)_2(Mg, Fe)_2Al_2(SiO_4)_3$.

(Cleavage $\parallel c$; curve a = muscovite, $t = 0.02$ and .04 mm.; curve b = biotite, $t = .03$ mm., Fig. 14.)

The constitution of the micas is involved in a greater or less degree of uncertainty. They are all silicates of aluminum and

[1] Clarke and Schneider, Amer. Jour. Sci., 40, 405, 1870.

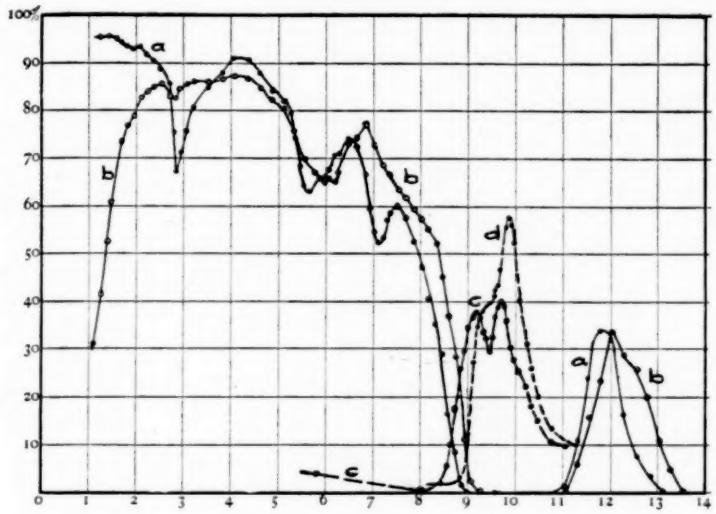

Fig. 14.

either K, Ba, Li or of Fe and Mg. All the micas yield water upon ignition, but it is uncertain whether this water of constitution is due to the presence of H or OH. There is no deep wide absorption band at 3 μ, so that judging by the present method of examination, there cannot be any hydroxyl groups present. Muscovite has a deep narrow band at 2.85 μ and smaller bands at 1.9, 3.6, 5.6, 5.9, 6.3 and 7.1 μ. Biotite has small bands at 2.8, 5.9, 6.2 and 6.7 μ, and indications of bands at 5.6 and 7 to 8 μ. It has also a band in the visible spectrum. Curves *c* and *d* are reflection.

Both micas have a large opaque region at 9 to 11 μ followed by a transparent region at 12 μ, beyond which there is again complete opacity. Rubens and Nichols[1] have found metallic reflection bands at 8.32, 9.38, 18.40 and 21.25 μ. It will thus be noticed that the bands located by the writer, by reflection and by transmission do not coincide, as is to be expected in a region of anomalous dispersion.

TALC, $H_2Mg_3Si_4O_{12}$.

(Subtransparent, $t = .06$ mm., curve *c*, Fig. 15.)

In talc water is expelled at red heat. From its stability with acids it is considered an acid metasilicate. From analyses of Clarke and Schneider (loc. cit.) no hydroxyl groups were inferred, and the

[1] Rubens and Nichols, Ann. der Phys. (3), 60, p. 418, 1897.

transmission curve does not show a band at 3 μ. Talc has absorption bands at 5.6, 5.95 and 7.15 μ.

SERPENTINE, $H_4(MgFe)_3SiO_9$.

(Massive, subtranslucent, curve *a*, $t = .225$ mm., $b = 0.08$ mm. From Montville, N. J., Fig. 15.)

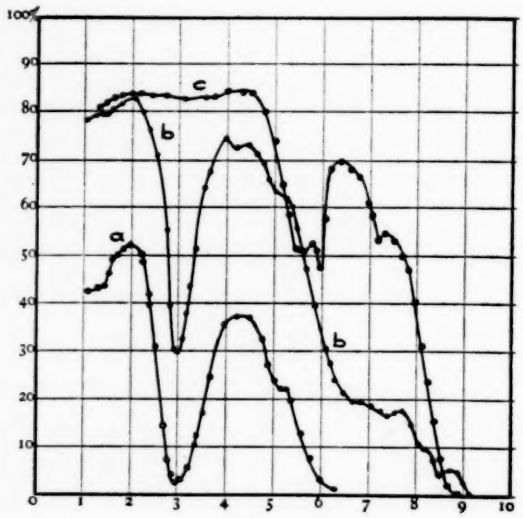

Fig. 15.

In serpentine the water is chiefly expelled at red heat. According to Miers [1] both talc and serpentine are to be regarded as basic and not hydrated silicates, since they part with their water only at a high temperature. From the curves of serpentine which show a large absorption band at 3 μ, if the results from the present method of examination are to be trusted, it would appear that there are hydroxyl groups present. From the analyses of Clarke and Schneider [2] it was inferred that the Mg is present as MgOH and hence the formula is written $H_3(MgOH)Mg_2(SiO_4)_2$. It has also been written with two magnesium hydroxyl groups. Serpentine has absorption bands at 1.4, 3, 5, 6.6, 7.4, 8.1 and 8.5 μ.

Group III., Miscellaneous Compounds; Sulphates.

It has been noticed elsewhere that in the examination of selenite the large absorption band at 4.55 μ is shifted and too deep to belong

[1] Miers, Mineralogy, p. 439.

[2] Clarke and Schneider, Amer. Jour. Sci., 40, p. 308, 1890.

to water; also that it was suspected to be due to the SO_4 groups of atoms. The band has further been noticed in discussing selenite and anhydrite, Fig. 3, and in thaumasite and blödite. Under the present heading will be discussed the absorption spectra of simple sulphates formed by the combination of a metallic oxide and sulphur trioxide, all of which show a band at 4.55 μ, while several have ahother band in common at 6.5 μ.

BARITE, $BaSO_4$.

(Orthorhombic, section $\parallel c$, translucent, $t = 0.25$, curve *a*, Fig. 16, from Cheshire, Conn.)

The barite curve is quite opaque due in part to numerous cracks. There are bands at 3, 4.6, 6.2, 6.5 μ. Königsberger's curves show that the band at 4.6 μ is wide and shifts for different directions of vibration of polarized light.

GLAUBERITE, $Na_2So_3CaSO_4$.

(Monoclinic, cleavage section $\parallel c$, transparent, $t = 1.26$ mm., curve *b*, Fig. 16.)

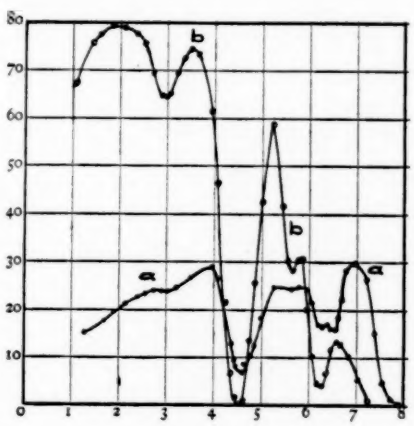

Fig. 16.

This is a mixture of two sulphates of which the $CaSO_4$ bands at 3.2 and 4.55 μ have already been noticed. Glauberite has bands at 3, 4.55, 5.6 and 6.2 μ.

THENARDITE, Na_2SO_4.

(Borax Lake, Calif. Orthorhombic, ground $\parallel c$, 2.2 mm.)

This material was too brittle to grind successfully. It shows a large band at 3.1 and 4.55 μ.

KIESERITE, $MgSO_4$.

(Stassfurt Mines. Massive, subtranslucent. $t = 0.22$ mm.)

This mineral, like selenite, shows both water and SO_4 bands. It is very opaque. The water bands at 1.5, 3, 4.55 (complex with SO_4) and 6.05 μ. There are two small bands at 1.8 and 7 μ, respectively.

CELESTITE, $SiSO_4$.

(Lampasao, Texas. Cleavage $\parallel c$, transparent. $t = 0.67$ mm.; curve *a*, Fig. 17.)

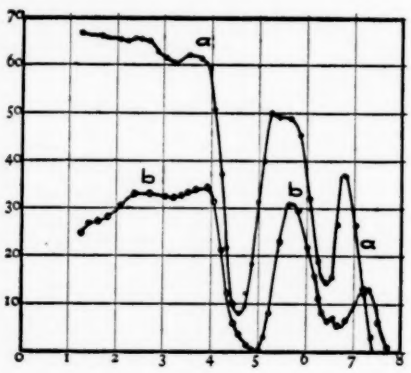

Fig. 17.

Celestite has absorption bands at 3.2, 4.55 and 6.4 μ. The 4.55 band is conspicuous for its great depth.

ANGLESITE, $PbSO_4$.

(Monte Poni, Sardinia; translucent, section $\parallel$ m. $t = 0.7$ mm.; curve *b*, Fig. 17.)

The section used was not quite long enough to cover the slit. The lack of transparency was in part due to the fact that on account of its brittleness the section was not highly polished. The band at 4.55 μ is complex, with a deeper one at 5 μ. The same is true of the 6.4 μ band, which is complex with a stronger band at 6.7 μ. There are slight depressions at 1.9 and 3.2 μ.

The examination includes various other compounds which would be too extensive to enumerate. At least 110 were examined,

and the spectrum of each mineral forms an interesting study by itself.

Part IV. consists of an investigation of reflection spectra of the aforesaid minerals which were of sufficient size to permit an examination. The silicates, *e. g.*, the feldspars and micas, show a region of selective reflection from 8 to 10 μ, some of the bands of which evidently are due to SiO_2. The sulphates have a region of selective reflection at 8.5 to 9.1 μ, the latter band being harmonic with the one at 4.55 μ.

The reflecting power of the sulphides of ZnFe and Sb are worthy of notice. They are known for their metallic lustre, especially Stibnite, Sb_2S_3. Their reflecting power in the infra-red is equally conspicuous for its high value, which is uniform throughout the region examined to 12 μ. Stibnite is the most marked in this respect. By transmission it was found to be unusually transparent, the absorption of a thin film, 0.4 mm., being about 44 per cent. throughout the whole region to 12 μ. The reflecting power was found to be about 43 per cent., so that the true absorption for this thickness is only some 2 or 3 per cent., which has been found in but few substances except gases.

The results obtained from the present examination of reflection spectra demonstrate a number of important facts. The first one is the dependence of reflection upon absorption. The second point worthy of notice is that region of selective reflection begins beyond 7 μ while for the majority of substances studied, the region of greatest activity is from 8 to 10 μ. Whether this coincidence in the grouping of reflection bands (of minerals other than those containing SiO_2) is fortuitous is unknown. A knowledge of their dielectric constants might aid in deciding this point. In considering this question of the selective reflection beyond 7 μ it will be recalled that the "general absorption" of many substances was found[1] to increase beyond this point.

The results as a whole show that in the silicates there are not such definite bands, whether found by reflection or by absorption, as one would expect. In other words, the silicon radical seems to

[1] "Investigations of Infra-red Spectra," Washington, 1905.

be differently bonded in each mineral. Possibly there are several radicals SiO_2, SiO_3, SiO_4, one or more of which are present in each mineral, or even in different specimens of the same mineral. This would explain the lack of constancy of the occurrence oft he bands of quartz of 3 μ.

The investigation has added one more radical which has definite absorption bands in the infra-red, *viz.*, SO_4, which has harmonic bands at 4.55 and 9.1 μ.

SUMMARY.

The transmission and reflection spectra of at least 120 compounds have been examined, many of them to 15 μ, by means of a mirror spectrometer, a rock-salt prism and a Nichols radiometer. The aim of investigation was the study of a series of minerals containing oxygen and hydrogen in the form of what is known as water of constitution and water of crystallization. The interpretation of the results are based upon the assumption that if the bonding of the oxygen and the hydrogen in the molecules is similar to that in ordinary water, then the absorption spectra of minerals containing these two elements thus bonded should show the absorption bands of water superposed upon the absorption spectrum of the other constituents.

On the other hand minerals containing oxygen and hydrogen as water of constitution should not show the water bands except hydroxyls which should show a band at 3 μ.

The results show that of some 30 minerals containing "water of crystallization" there are no important exceptions to the rule that they should show the bands of ordinary water. On the other hand the one important exception to the rule that minerals containing "water of constitution" should not show water bands is cane sugar. Minerals containing hydroxyl groups generally have a marked band at 3 μ. Sulphates have a strong band at 4.55 μ, and a less constantly recurring band at 9.1 μ, due to the SO_4 ion. On the other hand the silicates do not have such definite bands which would seem to indicate that the bonding of the silicate radical is different in each mineral containing that element. The examination includes minerals of which the chemical constitution is in doubt, for example, talc and serpentine. The former is not supposed to contain hydroxyl

groups, while in the latter such groups are inferred. The present examination supports these views in that the transmission curve of talc does not contain an absorption band at 3 μ, while serpentine contains a large band at 3 μ, which is in common with substances containing hydroxyl groups.

WASHINGTON, D. C.,
May 28, 1906.

THE COTEMPORANEOUS VARIATIONS OF THE NUCLEATIONS AND THE IONIZATION OF THE ATMOSPHERE OF PROVIDENCE.

BY LULU B. JOSLIN.

1. *Introduction.* — The results obtained by Professor Barus,[1] showing a characteristic succession of the values of atmospheric nucleation throughout the year, suggested a parallel inquiry into the variations of the number of ions in the atmosphere in the lapse of time. The present work which will appear in full in the Carnegie Publications, was therefore undertaken at his instigation, and observations systematically carried forward from August, 1905, to April, 1906.

In addition to the main purpose in view, it was hoped that a number of subsidiary questions might be answerable. Thus a large part of the nucleation of Providence is of local origin and enters the atmosphere with other products of combustion. Initially these nuclei were either highly ionized themselves, or the atmosphere originally received an accession of ions and nuclei in proportional quantities. It is therefore of interest to inquire whether any of the ionization survives, or whether there is any connection observable between corresponding changes of the nucleation and the ionization of a given place. The results which are carefully tabulated in the present paper seem to show that there is no such connection whatever; or that the ionization is maintained by causes which are quite distinct from those which bring forth the nucleation. No evidence suggests that the ionization is either emitted or absorbed by the nucleation, whence it follows that the ionization arises from agencies wholly nonlocal or artificial.

Apart from these main purposes, the data are interesting as a continuous record of ionization (which will be supplemented in the

[1] Smithson. Contrib., XXXIV., No. 1651, 1906, Chap. IX. Carnegie Publications, No. 40, January, 1906, Chap. IV. and V.

future), though as yet, sufficient time has not elapsed to ascertain whether the opposition in the monthly positive and negative ionizations found in the sequel is real or incidental. Cf. Fig. 5.

Finally I may add that work to investigate a possible relation between the nucleation and the ionization of the atmosphere, was undertaken in Helgoland and on the coast of the Ostsee by Prof. G. Lüdeling[1] in 1902 and 1903, using Aitken's dust-counter.

The time during which observations were recorded (August 21 to September 16, 1902, June 17 to July 4, 1903) were insufficient to warrant general conclusions, however, apart from the interesting special investigations which Professor Lüdeling's paper contains. Reference should also be made to P. Langevin's[2] important discovery of slow-moving ions in the atmosphere ; but comparisons of this nature are beyond my present purpose.

2. *Measurement of Nucleation.* — The number of nuclei in the atmosphere was measured by aid of the coronas of cloudy condensation, in the way fully described by Professor Barus (Smith's Contrib., l. c., Chap. 8) and the same apparatus which had proved efficient in the earlier investigations was used throughout the present experiments. Two or more observations were usually made daily, together with the meteorological elements of wind, weather and similar data. The ionizations referred below, § 7, were taken in the same place.

3. *Data for Nucleations.* — The tabulated data (which will here be omitted) show thc day and month, the time in hours and tenths of an hour, the current weather, the direction of the wind and the temperature of the atmosphere in degrees Fahrenheit, etc. Further data referring to the coronas give the temperature of the fog chamber in degrees C., the diameters, s, of the coronas at the end of a radius of 30 cm. Hence $s/30$ is nearly their angular diameter when the eye and the source of light are at distances 85 cm. and 250 cm. on opposite sides of the fog chamber. Final data indicate the colors of the successive annuli of the coronas, reckoned from within outward, and the number of nuclei in thousands per cubic centimeter

[1] Two papers in the Veröffentl. des Königlich Preussischen Meteorologischen Instituts, Berlin, 1904.

[2] P. Langevin, Bull. Soc. Franc. de Phys., May, 1905, p. 79.

deduced from the amount of water precipitated per cubic centimeter and the sizes of particles in successive coronas as listed by Professor Barus (l. c.).

TABLE I.

Average values, for successive months, of the number of nuclei, n, per cubic centimeter in the atmosphere of Providence, R. I.

Year.	Month.	$n \times 10^{-3}$	Year.	Month.	$n \times 10^{-3}$
1905	August.	22.9	1905	December.	50.3
	September.	24.2	1906	January.	53.3
	October.	35.3		February.	53.1
	November.	45.3		March.	52.6

4. *Remarks on the Table of Nucleation.* — With regard to the individual observations very little can be adduced that has not already appeared in the earlier work. Conformably with the mild winter, the nucleation as a whole is relatively low, an unfortunate occurrence in its bearing on the purposes of the present work; but deductions of this character will be brought forward with advantage in connection with the daily and monthly mean nucleations below. It is rather curious that the forest fires on Cape Cod in the early May and the powder combustion on July 4 produces so little impression; on the other hand, the cold weather in August is at once marked by large coronas.

5. *Mean Daily Nucleation.* — The data of § 3 were then averaged for the successive days in the second table. The results are recorded graphically at the bottom of the charts, Figs. 1 to 4, where the current days appear as abscissas, the corresponding mean nucleations in thousand per cubic centimeter as ordinates. One may note the rare occurrence of the large *g-b-p* coronas so frequently met in the high nucleations of the preceding winter.

6. *Mean Monthly Nucleations.* — The data of the last table suffice for the determination of the average nucleations per month, care being taken to omit the days on which no observations were taken. Table I. contains the results.

These data are shown in the lower graphs of Fig. 5. What is remarkable is the gradual rise of the curve to a persistent maximum reaching nearly into April. True the winter was relatively mild

and the spring relatively cold; but one would not be prepared to predict nucleations so uniformly maintained between November and April. The distribution is in fact peculiar, as may be seen by comparing it with the nucleation of the preceding years,[1] since 1902.

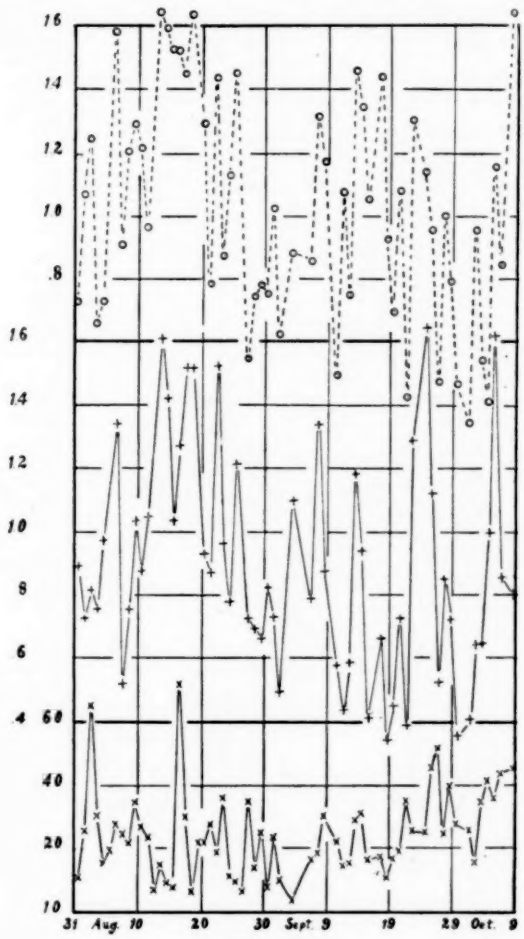

Fig. 1.

7. *Measurement of Ionization.* — To determine the number of ions in the atmosphere, Ebert's[2] well known apparatus was used. This consists of a tubular condenser, the inner coat of which is

[1] Barus, PHYS. REVIEW, XXII., 1906, pp. 91, 92.

[2] H. Ebert, Illustr. Aëronaut. Mittheilungen, Oktober, 1902, pages 1 to 10.

charged and in contact with a graduated electroscope. The air to be examined is passed through the condenser by an aspirator-fan propelled by clock-work. The air delivery of the machine is also carefully standardized.

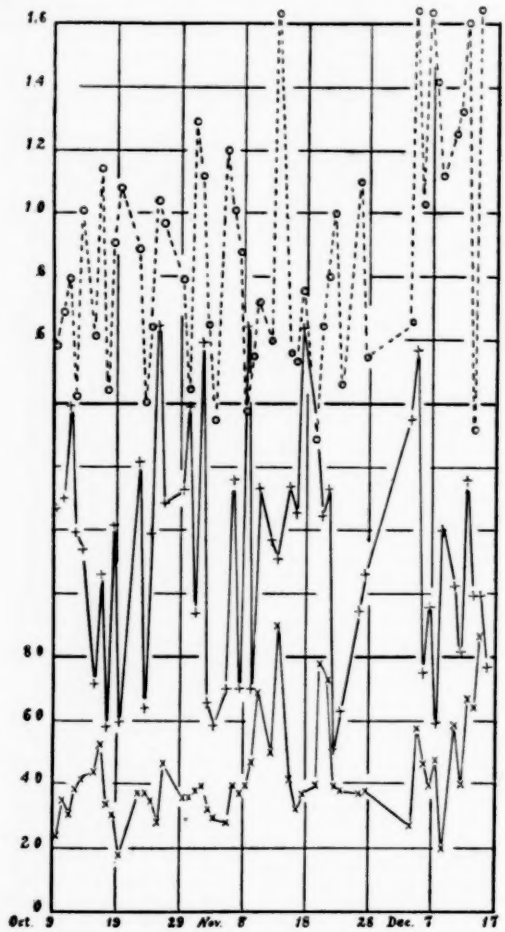

Fig. 2.

In order to test the same air which yielded the nuclei for the preceding measurement, the electrical apparatus was swung from the outside of a window on a long swivel bracket. In this way it could be drawn near the window for charging and examination with appropriate lenses, or moved to a reasonable distance away from the

window during the passage of the air to be tested. In winter all measurements must clearly be made with a galvanoscope on the outside of the house.

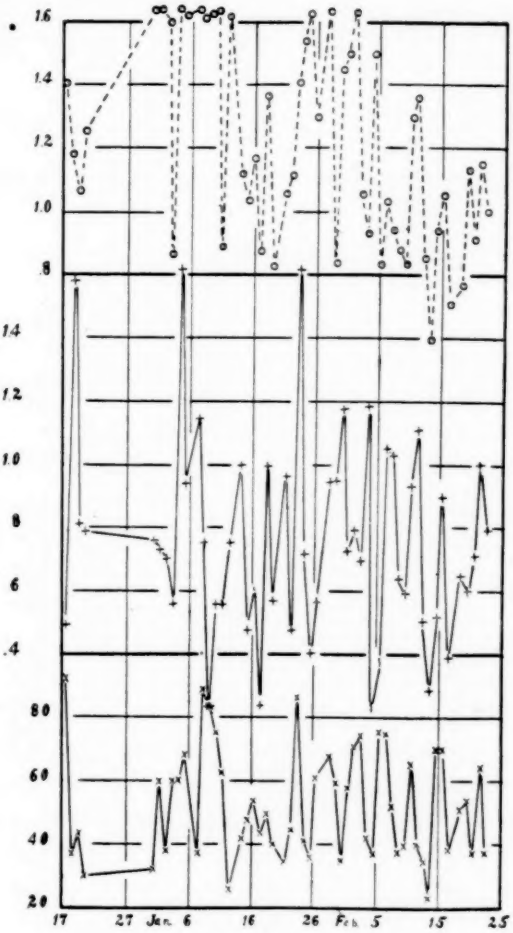

Fig. 3.

The difficulties encountered in using this apparatus in cold weather will be investigated later (§ 10). Here some reference to its constants is in place. The quantity of air passed through the condenser in the fiducial time (about 10 minutes) was 1.0357×10^6 cubic centimeters; the capacity of the condenser 17.74 cm. Hence if V is the drop of potential in volts during the fiducial time specified

$$Q = 17.74 \frac{V/300}{1.0357 \times 10^6} = \frac{V}{17.52 \times 10^6}$$

denotes the charge in one cubic centimeter of air. As 3.4×10^{-10} is the electrostatic charge per electron

$$n \times 10^{-3} = \frac{Q}{3.4 \times 10^{-7}} = \frac{V}{6}, \text{ nearly,}$$

shows the number of ions per cubic centimeter. Measurements to find their velocity were not made, as this would have carried me too far from the purposes of this paper.

I may add that a similar apparatus was installed, in which the winter indraft of cold air (through a condenser), measured by an anemometer, was utilized. The object here was to determine the hourly variations of ionization. Though many observations were taken their meaning is vitiated by the temperature discrepancy mentioned in § 10. For this reason, perhaps, a periodicity similar to the one discovered by Wood and Campbell [1] with stagnant air, was not detected. It need not, of course, be manifest with atmospheric air.

8. *Data for Ionization.* — The tabulated data contain the date and hour, the weather, etc., the fall of potential $V - v$ (v being the fall in the absence if the aspirator air current) in volts during the ten minutes of observation. From this the charge Q in electrostatic units per cubic meter, and the number of ions n, in thousands per cubic centimeter, were computed. The sign of the charges was indicated in each case, together with their ratio $(Q+/Q-)$. The correction v is regarded as negligible.

9. *Remarks on the Tables.* — Perhaps the most expeditious way of digesting this large body of observations is to plot them graphically (as above) in relation to time. This was carefully done throughout, and the statements now to be made refer to this summary.[2] It is not probable that positive and negative ions will show the same fluctuations in number, but a general similarity in the trend of the curves may be anticipated.

[1] Nature, April, 1906, p. 583.

[2] The daily means, Figs. 1–4, also elucidate the text.

Beginning with August, 1905, the positive and negative ionizations usually vary in the same sense though rarely in the same absolute magnitude. There being but two observations, as a rule, for the day, the nature of the fluctuations is not referable to periods;

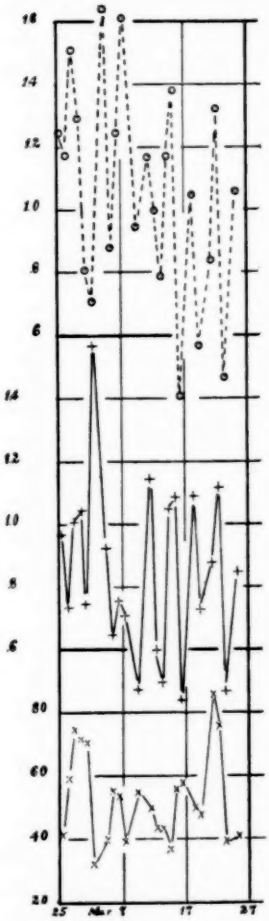

Fig. 4.

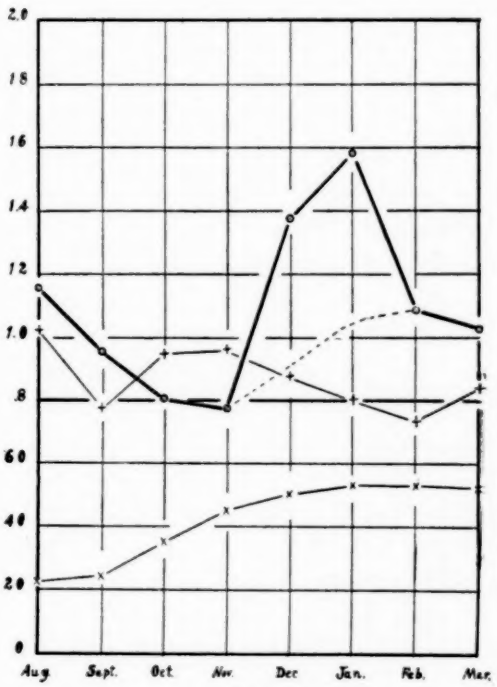

Fig. 5.

and indeed there is as liable to be a rise as a fall of values during the middle hours of the day. Towards the end of the month and in the beginning of September, there is an absence of agreement in the march of positive and negative ionizations. Frequently the variation of one ionization is apt to lag behind the other.

After the seventh of September the positive and negative variations tend to take the same sign again, but the agreement in the course of a month is less marked than before.

In October the earlier observations are as a rule in the same phase until October 10, where the first of a series of anomalies occur to be specially considered later (§ 10). While the data throughout the remaining part of October are regular, there are similarly displaced variations towards the end, which run quite into the next month.

During November similarity of variation of the positive and negative ionization may still be recognized, but in December the divergence of data is so marked that it is not possible to coördinate them; and the same discrepancy shows itself in January, both as regards the signs of variations and their absolute values. One may note moreover, that the positive curve, the observations for which were first taken, is more irregular in its march and fluctuates between relatively enormous values. Though there is some agreement in phase between January 18 and 25, the anomalies increase again at the close of the month.

The attempt was therefore made in February (§ 10) to account for and remove these discrepancies, and though this was but partially successful, the positive and negative results during the remainder of the season again return to an unmistakable agreement in character. There is moreover a curious parallelism between the general march of the nucleation curves and the ionization after February 15 as far as March. In the latter month the positive and negative ionizations, though at first fluctuating and uncertain, are finally in very close agreement.

From what has been stated it appears that the positive results during December and January are liable to be untrustworthy. The negative results, which were taken after the positive, show less irregular fluctuation and are in a measure acceptable throughout the eight months of observation.

10. *Errors of Measurement.* — The abnormal data during the occurrence of cold weather, and as a rule in December and January, show that some grave error must here have crept into the results. As every part of the condenser and appurtenances functioned fault-

lessly, this error is liable to be found in the galvanoscope. Changes of temperature produce vertical currents in the capsule which modify the deflections of the aluminum foils. In the mean ranges, one scale part of double deflection is equivalent to about six volts, or to one thousand ions per cubic centimeter. Hence the presence of any secondary disturbance like the one in question is of very serious consequence. Prior to measurement, the apparatus was naturally left in the cold air out of doors until temperature uniformity was presumable. But this is not sufficient as the special observations in the early part of February show, even for a galvanoscope dried with sodium.

Turning first to the leakages due to conduction, etc. (v in the above equation), direct experiments made at different times showed values of .073, .067, .120 volts per minute, or less than .9 volts for the ten minutes of observation. This is equivalent to an excess of 150 ions per cubic centimeter. As it is applied equally to the positive and to the negative ions, is independent of the size of the deflections and the same, no matter whether the deflections on both sides are equal or not, it has no bearing on the outstanding errors in question. It was not deducted from the ionizations n of Table I. which are therefore slightly too large.

Trials made between February 4 and 11 showed that in almost every case the first measurements (whether for positive or negative ions), even after the galvanoscope had been exposed to the cold air for some time, is too large. This discrepancy may at times extend to the second and third observations (February 6, 9, 11). Usually, however, the second and third observations are liable to be trustworthy (February 6, 10, 11, etc.). Hence electroscopic apparatus which cannot be left permanently out of doors, but is taken from a warm room into the cold atmosphere, even if it is sodium dried, is not liable to show warrantable results after mere waiting for uniform temperature. It seems additionally necessary to pass a large volume of cold air through the condenser, or to make successive measurements in series. The observer is usually in doubt, whenever the positive and negative ionizations differ widely, so that at least three tests must be made. The tendency of the apparatus to show spurious results is usually indicated by an inequality of deflections of the

foils on either side of the vertical. They may increase to a maximum after charging and then decrease regularly. The latter probably finds an explanation in the gradual cessation of down-pouring cold air current near the sides of the capsule of the galvanoscope, but the persistence of unequal deflections must follow from other causes. Remembering that the air is desiccated internally with metallic sodium, it seems hardly credible that there can be a precipitation of moisture from this dried air on the aluminum foils; and yet the behavoir is such as if a moisture gradient from the foil nearest the sodium to that more remote, were permanently maintained. In such a case there would be slight but unequal precipitation of vapor on the two foils, in an apparatus passing from warm to cold, and persistence would be due to freezing. The only other explanation is the possibility of charges on the very cold glass and other insulators which cannot be earthed.

11. *Mean Daily Ionization.* — As in the preceding case, the observations were now averaged for single days. The results appear in special tables, here to be omitted as they are sufficiently given in the charts, Figs. 1 to 4, where the number of ions in thousands per cubic centimeter are laid off vertically, the upper graph referring to positive, the middle to negative charge. Very little that is new may be taken from these figures and their appearance in this place is to serve as a basis for the monthly ionizations which follow. In comparing the ionizations with the nucleation of the atmosphere, however, these charts serve a useful purpose. Thus it would be difficult to detect synchronism in the nucleations and ionizations of August, September, October, November, December. But from the middle of January to the end of February suspicions of this kind would be justified.

12. *Mean Monthly Ionizations and Conclusion.* — The straightforward way of arriving at a conclusion as to the presence or absence of a relation between the nucleation and the ionization of the atmosphere, consists in comparing the average monthly values for both cases. This is done in Table II., and graphically in Fig. 5.

The curve showing the distribution of negative ions is probably the more trustworthy, as these observations were made last. The positive distribution curve is too high in December and January

for the reasons already stated, and its more probable course during these two months is indicated by the dotted line. It seems exceedingly curious, that whereas the fluctuations of positive and negative ionization in successive observations on the same or on succeeding days, usually show the same sign though not the same absolute value, this is not in general the case with the monthly ionizations. The two curves of Fig. 5 throughout the greater part of their course vary in opposite directions.

TABLE II.

Average values, for successive months, of the number, n, of positive and of negative ions per cubic centimeter in the atmosphere of Providence, R. I.

Year.	Month.	$n \times 10^{-3}$ (positive ions).	$n \times 10^{-3}$ (negative ions).
1895	August.	1.16	1.02
	September.	.95	.78
	October.	.80	.95
	November.	.78	.96
	December.[1]	1.38	.88
1896	January.[1]	1.58	.80
	February.	1.09	.74
	March.	1.03	.84

Compared with the uniform curve for nucleation, the appearance of the ionization curve is sufficiently distinctive. The only conclusion to be drawn from the results for the distribution of either the positive or the negative ions is this, that there is no discernible relation between the number of ions and the number of nuclei present in the atmosphere at any time, or that the two distributions result from entirely distinct causes. The ionization of a given region in the long run is independent of artificial local contributions, however abundant these may be.[2]

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[1] See § 10.

[2] As the negative ions are more easily "absorbed" by the nuclei than the positive ions, one might refer the descent of the graph from November to February to some such cause; but the curve as a whole does not bear this out consistently.

THE CADMIUM STANDARD CELL.

BY GEORGE A. HULETT.

A STANDARD cell with a low temperature coefficient was devised by Mr. Edward Weston in 1891.[1] By substituting cadmium sulphate and cadmium amalgam for the zinc sulphate and zinc of the Clark cell, it was found that the temperature coefficient of the cell was reduced 95 per cent., and when the solid cadmium sulphate was dispensed with and only a solution of cadmium sulphate used in the cell, the temperature coefficient was still less. With a solution saturated at 0° C., Barnes and Lucas found[2] that the E.M.F. of the cell was constant for all ordinary temperature changes. This latter combination is a valuable laboratory instrument, but is not sufficiently reproducible or constant to serve as a standard of E.M.F.

The Clark cell has a variation of E.M.F. of over a millivolt per degree, and for accurate work requires a very exact control of the temperature for a considerable time. The saturated cadmium cell has only one twentieth of the temperature coefficient of the Clark cell and many other desirable features, so that considerable work has been done in testing its reproducibility and constancy.

A. Dearlove[3] found that attention must be given to the cadmium amalgam and concluded that it was best to use a 12.5 per cent. amalgam, made by melting together one part of cadmium and seven parts of mercury. Since then considerable work has been done on cadmium amalgams. Kerp and Boettger[4] concluded that the solid which separates from cadmium amalgams of over 5 per cent. was a compound represented by the formula Cd_2Hg_7. However, from the work of Bijl[5] and Puschin[6] it appears that between about 5 and 15

[1] U. S. Patent No. 494,824. Applied for April 24, 1891.
[2] Jour. Phys. Chem., 8, 196, 1904.
[3] Electrician, 31, 645, 1893.
[4] Zeit. f. Amorg. Chem., 25, 1, 1900.
[5] Zeit. Phys. Chem., 41, 641, 1900.
[6] Zeit. f. Anorg. Chem., 36, 201, 1903.

per cent. of cadmium, the amalgam is a two-phase system, composed of a solid and a liquid phase, and that the solid phase is not a compound, but an isomorphous mixture of cadmium and mercury. The composition of this mixed crystal varies with the temperature, but has a definite composition and E.M.F. for each temperature. The result is that on adding cadmium to mercury, the E.M.F. of the amalgam, towards a cadmium sulphate solution, increases with the increasing per cent. of cadmium until the mixed crystal appears. If the temperature is constant, further additions of cadmium will not effect the E.M.F., but only the relative amounts of the two phases. When the liquid phase disappears a further addition of cadmium will increase the E.M.F. of the system. From Bijl's results this two-phase range is between 10 and 18 per cent. of cadmium at 50°, 5.3 to 15 per cent. at 25° and 4 to 14 per cent. of cadmium at 18°. Jaeger[1] showed that all amalgams in a two-phase range have, for a given temperature, the same E.M.F. almost to the limit of measurement, and it is this property that makes the cadmium amalgam valuable for a standard cell, since little attention need be given to the exact composition of the amalgam, only that it must always remain in the two-phase range for all temperatures at which the cell is used. The 12½ per cent. amalgam first proposed by Dearlove, l. c., satisfies these conditions and also has the desired solidity.

It will be concluded from the above that there must be a temperature coefficient for the E.M.F. of the junction: Cd-amal. || cadmium sulphate solution. To test this the following combination was set up:

Cd amal. 0° C. || $CdSO_4$ solution sat. at 4° || Cd-amal. 30° C.

This showed a thermoelectomotive force of .00917 V. in the direction of the arrow, also the following combination:

mercury 0° C. | Hg_2SO_4 | cadmium sulphate solution sat. at 4° C. | Hg_2SO_4 | mercury 30° C.

showed the same .00917 V. and in both cases the cold metal was the anode. Therefore both legs of the cadium cell have a decided temperature coefficient, but when the directions of the electromotive forces at the two electrodes are considered, it will be seen that the

[1] Wied. Ann., 65, 106, 1898.

two temperature effects are oppositely directed as far as the total E.M.F. of the cell is concerned, and it is merely a coincidence that the E.M.F. of the cadmium cell is so little affected by temperature changes.

The amalgam may be made by depositing cadmium electrolytically in a weighed amount of mercury. An excess of cadmium is deposited, the amalgam weighed, and then the correct amount of mercury added to make it 12.5 per cent. Very pure cadmium is obtained in this way if recrystallized cadmium sulphate is used for the electrolyte. This method was devised and used for the amalgams of the (*D*) and (*F*) cells of 1903 but it has since been found that a trace of other metals, even zinc, has hardly a measurable effect on the E.M.F. of the cadmium amalgam and that ordinary pure cadmium answers every purpose. The later amalgams have been made by melting together one part of Merck's cadmium with 7 parts of pure mercury, and this was done on a water-bath with the metals covered with a cadmium sulphate solution.

Cadmium sulphate ($CdO_4 8/3 H_2O$) is a well-defined salt and is easily obtained in large monoclinic crystals which do not seem to carry other salts isomorphously mixed.[1] The rate of growth of the crystals is very slow and the clear ones are quite free from inclusions, but in every crop there are many white crystals which grow more rapidly and may have inclusions. It is an easy matter to pick out the clear crystals and, due to their slow rate of solution, they may be thoroughly rinsed with water. In the work so far the cadmium sulphate crystals have been dissolved by grinding them in a mortar with water until a saturated solution was obtained. This solution was treated with a little cadmium carbonate to neutralize any excess of acid which might have been present. The solution was then carefully filtered and placed in a crystallizing dish to a depth of one centimeter, the dish was covered with thin filter-paper to keep out dust and the solution allowed to evaporate until a good crop of crystals formed. Samples of cadmium sulphate from various sources and with known impurities have been used, but it has been found that, after one crystallization and thorough rinsing that there was not a detectable difference in their behavior of the clear crystals in

[1] Retgers, Zeit. f. Phys. Chem., 16, 594, 1895.

cadmium cells. The solution from these crystals is slightly acid as the result of hydrolysis, but the solution of these crystals in distilled water is exceedingly well-defined and reproducible and it has been found unnecessary and undesirable to change it in any way. Kohnstamm and Cohen[1] thought that they had detected a transition point for this salt at 15° C. but the changes on which they based their conclusion have been traced to the 1 to 6 amalgam used.[2] This strength amalgam is not a two-phase system below 23° and may undergo slow changes.

The mercury used in all this work on standard cells has been distilled under diminished pressure with a current of air passing through with the mercury vapor. This method insures the removal of all oxidizable metals.[3]

The Depolarizer.

The most extensive observations on the cadmium cell have been published by Jaeger and Lindeck.[4] From their results it seemed that the cadmium cell was reproducible to 1 or 2 parts in 10,000 and the authors attributed the observed variations to the fact that the mercurous sulphate used as polarizer was from different sources, just as Lord Rayleigh had previously[5] traced variations in the Clark cell to differences in the mercurous sulphate.

Commercial mercurous sulphate is usually made from solutions of mercurous nitrate and sodium sulphate. The precipitate is exceedingly finely divided and carries with it traces of the reagents and is acid. Also an insoluble basic salt is formed and, while these impurities are not present in large quantities, they increase the mercury in the solution made from such preparations and give too large a value to the E.M.F. of the cell.

A fine-grained powder is more soluble than a coarser-grained sample of the same salt, and while the fine-grained powder slowly becomes coarser-grained when left in contact with its solution, there is here a possible source of variation, as has been pointed out by

[1] Wied. Ann., 65, 344, 1898.

[2] Cohen, Zeit. Phys. Chem., 34, 631, 1900, and Jaeger and Lindeck, Zeit. Instk., 21, 33, 1900.

[3] Phys. Rev., 21, 387, 1905.

[4] Zeit. f. Instk., 21, 33, 1901.

[5] Philos. Trans., 176, 781, 1886.

H. v. Steinwehr.[1] The "Board of Trade" specifications advise the washing of the mercurous sulphate with water, and while this removes some of the impurities, it also hydrolyzes some of the salt. A rather insoluble basic sulphate is left with the salt, while a soluble acid salt goes into solution, and the wash water with the acid salt is not entirely removed even by suction. It will be seen that the materials and methods which have been used in making the paste for cells afford abundant opportunity for variations. Experiments have shown that acids and particularly the basic salt cause irregular variations in the E.M.F. of the standard cells.

In 1903 the electrolytic method of preparing mercurous sulphate was devised by the author[2] and independently by Dr. F. A. Wolff, of the Bureau of Standards.[3] By this method pure mercurous sulphate, mixed only with dilute sulphuric acid and mercury, was obtained. The acid was removed either by washing with the saturated solution of cadmium sulphate or by using alcohol and ether. Both methods were effective in removing the acid and seemed to prevent hydrolysis. The first cells made with this properly washed electrolytic mercurous sulphate were four (*D*) cells on December 21, 1903, and 10 (*F*) cells on February 15, 1904. These cells agreed among themselves to 1 part in 100,000, assumed their constant value at once but were .00028 V. lower than cells made in the old way with commercial mercurous sulphate.

These cells seemed so much superior to those made according to the old specifications that attention was at once turned to thoroughly testing samples of mercurous sulphate made by the electrolytic method. In brief it was found that it was possible to use a very considerable range of acid strength and current density in making the sulphate. Also that the preparation was sufficiently coarse-grained to entirely avoid any effect due to the size of particles on the solubility, and that it was the most reproducible and reliable preparation for use in standard cells. The details of this work as well as a complete description of the method of preparing electro-

[1] Zeit. f. Instk., 25, 201, 1905.

[2] Trans. Amer. Electrochem. Soc., 5, 59, 1904; Trans. Internat. Elect. Congress St. Louis, Vol. 2, 109, 1904; Zeit. Phys. Chem., 49, 483, 1904.

[3] Trans. Amer. Electrochem. Soc., 5, 49, 1904.

lytic mercurous sulphate and making the paste for cells have already been described.[1]

Slow Changes in the E.M.F. of the Cadmium Cell.

After the (*D*) and (*F*) cells have been under observation for nearly two years, six cadmium cells, *A*1 to *A*6, were made and the materials and construction were, as nearly as it was possible to make them, a duplication of the (*D*) and (*F*) cells, *but these new cells were .00011 V higher than the older ones.* More cells were made with different samples of electrolytic mercurous sulphate and with variations in the other materials and in the construction, but they all agreed with the new (*A*) cells. Fortunately 10 Clark cells had been made in 1904, and with some of the same electrolytic mercurous sulphate which had served for the depolarizer of the (*F*) cells. These Clarks did not show the usual "ageing" but appeared to have their constant value at once. After two years, however, they appeared to have slightly increased in value (.00011 V.). The cadmium cells had been assumed constant and had been made the basis of all the comparisons. If now the Clarks had been assumed to be constant and taken as the basis, the cadmium cells would, of course, appear to have decreased by this .00011 V. and the difference between the new and the old cadmium cells is then explained by a slow change in the cadmium cell.

More Clark cells (*H*11 to *H*16) were made on July 30, 1905, and on February 25, 1906, cells *H*17 to *H*21 were made, and for depolarizer some of the same sample of electrolytic mercurous sulphate was used as had served for the new (*A*) cells. The following table gives some of the many observations that have been made on these cells. All the cells have been maintained in a large oil-bath since October, 1905. The bath was electrically heated and controlled and the temperature has remained constantly at 25° C. to within $\frac{1}{50}°$. For details see this journal, 22, 323, 1906. The basis of all the results given in this paper are the Clark cells, *H*1 to *H*21, which were made on three different dates and are now in good agreement. The value chosen is the one obtained by Dr.

[1] Phys. Rev., 22, 321, 1906.

Guthe for these cells and is 1.42040 V. at 25° C.[1] This gives a calculated value of 1.43300 at 15° but it should be added that these Clark cells were all made with electrolytic mercurous sulphate as depolarizer; the paste was prepared as previously described,[2] and they are .00030 V. lower than Clark cells made in the old way with commercial mercurous sulphate.

Cell.	Date.	Mar. 18, '04.	Mar. 24, '05.	Aug. 5, '05.	Dec. 14, '05.	Mar. 4, '06.	June 4, '06
*D*4	Dec. 21, '03.	1.01842	1.01831	1.01928	1.01832	1.01832	1.01830
*F*1	Feb. 15, '04.	42	31	27	30	32	29
*F*2	"	42	32	26	31	30	15
*F*3	"	42	32	28	32	31	34
*F*4	"	42	31	28	32	32	27
*F*5	"	42	32	32	31	33	33
*F*6	"	42	32	27	32	33	32
*F*7	"	42	32	28	34	32	32
*A*1	Oct. 21, '05.				1.01843	1.01843	1.01842
*A*2	"				43	43	42
*A*3	"				42	43	42½
*A*4	"				43	43	42½
*A*5	"				43	43	42½
*A*6	"				43	43	43
*H*2	Mar. 15, '04.	1.42040	1.42040	1.42038	1.42038	1.42040	1.42039
*H*3	"	40	37	38	—	40	39
*H*4	"	40	38	37	40	43	42
*H*6	"	39	—	42	37	40	42
*H*7	"	41	41	44	38	40	40
*H*8	"	41	40	41	—	40	40½
*H*11	July 30, '05.				1.42040	1.42041	1.42039
*H*15	"				41	41	41
*H*16	"				41	41	42
*H*17	Feb. 25, '06.					1.42039	1.42041½
*H*18	"					39	42
*H*19	"					40	42
*H*20	"					38	37
*H*21	"					43	41
*C*1	Nov. 21, '03.	1.01868	1.01864	1.01858	1.01862	1.01861	1.01860
*A*7	Nov. 15, '06.				72	70	67

The results given in Table I. from December 14, 1905 on, are the observed values, but the values for March 18, 1904, March 24,

[1] PHYS. REV., 21, 117, 1906.

[2] PHYS. REV., 22, 334, 1906.

1905, and August 5, 1905, have been recalculated, for the sake of comparison, from the observations which were made at 21° and 18°. These cells all follow the accepted temperature coefficient so closely that the calculated values are reliable, but the conclusive facts are based upon the observations made since October, 1905, when the control of the temperature and the conditions of comparison have been particularly exact.

It is to be observed that the new cadmium cells, *A*1 to *A*6, are now .00011 V. higher than the older (*F*) series, and that the values of the (*A*) cells are now very close to the values the (*F*) cells originally had. On the other hand the Clark cells, made on three different dates, are now all in excellant agreement. The depolarizers of the (*F*) cells and the *H*1 to *H*10 Clarks were all from the same sample, while the sample of mercurous sulphate which was used for the new *A*1 to *A*6 cells was also used for the Clarks *H*17 to *H*21. This indicates that the change observed in the (*D*) and (*F*) cells is not a peculiarity of the electrolytic mercurous sulphate. Further proof that the electrolytic mercurous sulphate is not at fault is at hand in the observations on some cadmium cells which were made in 1903 with commercial mercurous sulphate according to the old specifications. These cells have also changed as indicated by the record of cell *C*1 given in Table I. On November 15, 1905, cell *A*7 was made with commercial mercurous sulphate and according to the old specifications and it will be seen that this cell is now higher than the older (*C*) cell. All of the cells made with commercial mercurous sulphate and according to the old specifications were very high at first and showed the usual "ageing" for a month before becoming "constant."

In the literature there is some evidence of this "drift" of the cadmium cell, Mr. F. E. Smith[1] describes some cadmium cells which were made in April, 1902, and two years later another cell was made with exactly the same materials, but the new cell was .00007 V. higher than the older ones.

This observed change in the E.M.F. of the cadmium cell is small and slow and from a practical standpoint is of little consequence, but it is not to be overlooked when it comes to a question of a

[1] Electrician, 53, 832, 1904.

standard of electromotive force. The change seems to be more rapid at higher temperatures and especially does the depth of the paste in the leg of the cell play an important rôle. Some cells were made on November 29, 1904, with the paste only 3 or 4 mm. deep, the object was to make a cell with a smaller internal resistance. These cells showed the normal value of 1.01844 V. when first made, but began at once to noticably decrease. On January 10, 1905, they were 1.01839, April 4, 1905, 1.01811 and by June, 1905, were about 1.0177 V. and were very irregular, only two of these cells were retained and in December, 1905, they were 1.0172 and 1.01815, and now June, 1906, they are 1.0160 and 1.01813 respectively. It is to be noted that the (*F*) cells are no longer in as good agreement as when first constructed. The paste in the (*F*) cells is about 10 mm. deep and it is 20 mm. deep in the *A* cells and in all cells made since these facts appeared. It might be added that the (*A*) cells have not yet shown a decided change but it is probably only a question of time.

From the foregoing it is to be concluded that slow changes take place in the cadmium cell and, during the past two years, a number of results have been obtained which indicate that it is the system in the cathode leg of the cell which is not in equilibrium. Mercurous sulphate has been formed electrolytically in a cadmium sulphate solution. The apparatus and method was the same as used for preparing electrolytic mercurous sulphate.[1] The mercury from the anode went into the cadmium sulphate solution and separated as mercurous sulphate while cadmium was deposited at the cathode, the solution remained neutral and was saturated as cadmium sulphate crystals were present. The idea was that this preparation might be used directly in the cell without removing the mother liquor. It was expected that with this method and the rapid stirring that the product obtained would be in equilibrium with the cadmium sulphate solution and the mercury. Two samples were prepared and different current densities were used. The preparations were white and sufficiently coarse-grained to avoid the effect of size of particles on the solubility. One sample was made with a current density of .12 amp. per 100 cm.^{2} mercury anode surface,

[1] PHYS. REV., 22, 334, 1906.

and was used, with some of the solution in which it was made, for the depolarizer of cell $A17$. Some of this same sample was used for cell ($A18$) but its solution was first removed by suction and then it was washed with a fresh cadmium sulphate solution. The second sample was made with a current density of .5 amp. and was used direct in cell $A19$. These cells were made November 23, 1905, and the following results have been obtained:

Cell.	Nov. 30.	Dec. 14.	Jan. 1, 1906.	Feb. 7.	Mar. 4.	Apr. 13.	May 12.	June 4.
$A17$	1.10878	1.01872	1.01871	1.01870	1.01873	1.01871	1.01869	1.01868
$A18$	86	78	75	67	65	60	58	55
$A19$	48	48	47	49	48	49	48	48

It will be seen that the samples made with the different current densities do not agree and that the one made with the larger current density ($A19$) has remained quite constant and is nearest to the $A1$ to $A6$ cells. The sample which was made with a low-current density was used in cell $A18$, but the solution in which it was made was first removed by suction and then the salt was washed with a fresh cadmium sulphate solution. This cell was high at first and has decreased the most.

Two years ago an attempt was made to bring mercurous sulphate into equilibrium with a cadmium sulphate solution and mercury. The system — cadmium sulphate, mercurous sulphate, mercury and saturated solution — was rotated at 25° for ten days, and then the mercurous sulphate was brought onto a filter and washed with a fresh solution of cadmium sulphate. With this preparation three cells were made on May 6, 1904, and the following observations, calculated to the present basis and 25°, have been made:

Cell.	May 6.	May 9.	June 13.	July 13.	Aug. 9.	Apr. 14, 1904.	June 3.	July 25.
/6	1.01975	1.01934	1.01900	1.01889	1.01887	1.01817	1.01800	1.01816
/7	77	32	01	88	91	15	1797	1799
/8	63	31	03	93	96	32	1807	1818

The cells had become irregular and had not become constant and it was concluded that the system, which had been rotated ten days, had not reached equilibrium, so the observations on these cells were discontinued. This question was taken up again after the "drift"

in the (*D*) and (*F*) cells has been detected. It was decided to rotate this system in the cathode leg until it should come to equilibrium. When this point is reached there should be no further change in the solution or in the E.M.F. between the system and mercury. It was found most convenient to measure the E.M.F. at frequent intervals as a means of deciding on the absence of further change in the system.

An adjustable cadmium cell was made as represented by Fig. 1, the leg (*A*) contained the cadmium amalgam and the cadmium sulphate of the anode, and it will be seen from the cut that the side tube (*B*) of this leg bends down and passes through the neck of the tube (*C*). This tube (*C*) contained the mercury, paste and cadmium sulphate of the cathode leg of the cell. This cell was used in a water-bath and it was found necessary to attend to the insulation.

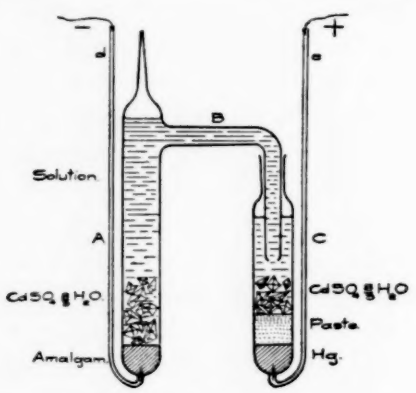

Fig. 1. ($\frac{1}{3}$ nat. size.)

Fig. 2. ($\frac{1}{6}$ nat. size.)

This was done by sealing on the little tubes (*e*) and (*f*) as indicated in the cut, the contact wires passed up through these tubes and there was then no further trouble on this point. This cell had the value 1.01837 and has remained perfectly constant, although it has many times been taken apart and the anode leg used to test other systems. The cell is now six months old and a new anode leg has lately been made, but it shows exactly the same value as the older ones.

A large tube, 5 × 24 cm. (Fig. 2), contained the materials of the cathode system of the cadmium cell. The neck of this tube was made to admit the side tube (*B*) of the adjustable anode (*A*), Fig. 1,

thus forming a cadmium cell. Contact with the mercury in this large tube was made through a platinum wire which was fused through the closed end of the tube and passed up on the outside. The wire was covered with shellac, a thin strip of cloth was placed over the wire and then it was thoroughly shellaced and finally covered with a coat of collodium (the use of collodium was suggested by Dr. E. H. Loomis and is a very admirable device for protecting anything which is to be in contact with water for any length of time). This large tube contained 140 gr. of mercury, 50 grams of coarse-grained electrolytic mercurous sulphate which had been washed with alcohol and dried, 50 gr. of cadmium sulphate crystals and about 400 c.c. of a saturated solution of cadmium sulphate. In order to bring this system to equilibrium, the neck of the tube was securely closed with a cork and rubber covering, the tube was brought to a horizontal position in the 25° bath and rotated about its longer axis as follows: Above the bath was a shaft which was run at any desired speed by a worm gear, and from this shaft two little belts extend down into the bath. The tube was suspended in the loops of these belts. The belts were kept in place by rubber rings on the shaft and on the tube. In this way it was possible to rotate the tube about its longer axis at any desired speed, the solid contents of the tube were spread out in a long layer and slowly "rolled down hill" as the tube rotated. This method insured a thorough mixing of the contents of the system and was sufficiently gentle to avoid grinding the solids. A fine powder has an abnormal solubility and this error is very considerable when the solubility is small. Also it was found desirable to avoid breaking up the mercury into small globules, because these globules formed larger ones when the rotation was stopped, and this change caused very decided variations in the E.M.F. readings. It was found that by rotating the tube at the rate of one revolution in about six seconds that the mercury generally remained in one globule, and that this rate, with the above method, still insured a perfect mixing of the contents of the tube. From time to time the tube was brought to an upright position in the bath and the E.M.F. measured with the aid of the adjustable anode leg. The large 100 liter thermostat maintained the temperature constantly within .02° of 25° C. Since the rotat-

ing would unduly expose the mercurous sulphate to the light, it was decided to avoid this possible source of error by covering the tube with asphalt paint and then with collodium.

The first rotation was for twelve hours, when the system was tested with the anode leg the first reading

3	minutes	after	stopping the rotation	was 1.0190 V.
9	"	"	"	1.0184
35	"	"	"	1.0178
3	hours	"	"	1.0177

The system was now rotated three days and

5	minutes	after	stopping the rotation	the E.M.F. was 1.01938 V.
20	"	"	"	1.01942
1	hour	"	"	1.01941
5	"	"	"	1.01941

The tube was closed and rotated seven and one half days, making a total of eleven days.

3	minutes	after	stopping the rotation	the E.M.F. was 1.01820 V.
9	"	"	"	1.01860
30	"	"	"	1.01910
3	hours	"	"	1.01971
24	"	"	"	1.01971

The preliminary low values observed here were regarded as due to the mercury being in small globules and as they united to form larger ones the E.M.F. increased to a maximum. That the constant value obtained was reliable is shown by the following test. Some of the clear solution was removed and brought into a tube like the tube (*C*) of Fig. 1. Some mercury was put in to serve as an electrode and then the solution tested with the anode leg. The value obtained was 1.01983.

The system was now rotated six and one half days, making a total of seventeen and one half days.

3	minutes	after	stopping the rotation	the E.M.F. was 1.01920 V.
5	"	"	"	85
30	"	"	"	91
1	hour	"	"	89
5	"	"	"	90
24	"	"	"	79
72	"	"	"	74

The clear solution was tested as previously described and gave 1.01992 V. Evidently a change begins to take place in the layer next to the mercury as soon as the solids settle down on the electrode and this is possibly the "drift" of the cadmium cell at its maximum rate.

The tube was again closed and rotated for eight and one half days, making a total of 26 days. The following readings were then obtained:

3	minutes	after	stopping	the rotation	the E.M.F. was 1.0120 V.
6	"	"	"	"	1.0155
18	"	"	"	"	1.0166
1	hour	"	"	"	1.01910
3	"	"	"	"	1.01976
7	"	"	"	"	1.01977
24	"	"	"	"	1.01973
48	"	"	"	"	1.01967
170	"	"	"	"	1.01948

Here the preliminary low value, which has been attributed to changes in the mercury electrode, was more persistent and the maximum value observed was consequently lower. After the tube had stood quietly for a week, the lower end was given a rotary motion in order to break up the mercury into smaller globules but without mixing the entire contents of the tube.

2	minutes	after	the shaking	just mentioned	the E.M.F. was 1.0135 V.
7	"	"	"	"	1.0161
12	"	"	"	"	1.0177
45	"	"	"	"	1.0196
1	hour	"	"	"	1.01985
2	"	"	"	"	85
6	"	"	"	"	85

These results indicate that the preliminary low values observed in the preceding experiments were due to the mercury changing from small to large globules, as had been assumed. It was possible to still further test this point as follows. The tube was rotated as before for three and one half days at the rate of one revolution in six seconds and then the rate was decreased to one revolution in seventy seconds and this rate of rotation was continued for one day in order to allow the mercury to collect in one globule. The tube

was then carefully brought to an upright position and the anode leg adjusted.

2	minutes	after	stopping	the rotation	the reading was 1.01977 V.
4	"	"	"	"	77
10	"	"	"	"	78
40	"	"	"	"	76
1½	hours	"	"	"	75
5	"	"	"	"	71
9	"	"	"	"	68
24	"	"	"	"	64
48	"	"	"	"	

The clear solution gave 1.01985. It is evident from the preceding experiments that if the system in the cathode leg of the cadmium cell is stirred until no further change takes place that, at 25°, the cell has the value 1.0198 V. or .0014 V. higher than the cadmium cell. If this system, after it has been rotated until no further change takes place, be allowed to rest, the E.M.F. begins to drop but the clear solution, from which the solids have settled, continues to retain its high E.M.F. against a mercury electrode. It seems reasonable to conclude that there is some interaction between the cadmium sulphate solution and the mercurous sulphate which produces an increase in the mercury concentration of the solution, but when the solids settle down on the mercury, another change takes place at the boundary between the mercury and the paste which causes a decrease in the mercury concentration of solution next to the mercury. The possibility, that the oxygen of the air dissolved in the solution produces some mercuric mercury, has been considered. This would explain the results obtained if we assume that the mean rate of oxidation is rapid compared to the subsequent rate of reduction by the mercury. However I have not been able to get experimental proof of this view, while the following results with the cathode system of the Clark cell show that under similar conditions, oxidation by dissolved air does not play a measurable rôle in the case of a zinc sulphate solution. It seems more probable that the interaction between the cadmium sulphate solution and mercurous sulphate is of the nature of an hydrolysis accompanied by the slow formation of a new, slightly soluble solid phase. The evidence for this view will be given when the present experiments are completed.

In order to test the method that has been employed in the preceding experiments and also to confirm many of the conclusions, it was decided to subject the cathode system of the Clark cell to the same processes. An adjustable Clark cell was made similar to the above adjustable cadmium cell. This Clark cell has shown a constant value of 1.42045 V. at 25°. A large rotating tube was charged with mercury, mercurous sulphate (electrolytic washed with alcohol and dried), recrystallized zinc sulphate, and the saturated solution. This system was rotated as previously described and after twelve hours the contents were tested with the adjustable anode of the Clark cell, with the following results:

3 minutes	after	stopping	the	rotation	the E.M.F. was 1.42052 V.
45 "	"	"	"		1.42048
3 hours	"	"	"		1.42048
6 "	"	"	"		1.42049

The system was now rotated twenty-four hours and then showed 1.42050 V. and after the solids had settled some of the clear liquid was tested against a mercury electrode with the adjustable anode and the value obtained was 1.42051 V.

The system was now rotated for six days.

3 minutes	after	stopping	the	rotation	the E.M.F. was 1.42055 V.
6 hours	"	"	"		1.42050
27 "	"	"	"		1.42054

The tube was again closed and rotated for 10 days, making a total of seventeen and one half days, and then gave the value of 1.42052 V. and was constant. This experiment shows that the cathode system of the Clark cell comes to equilibrium in less than twelve hours and remains constant from then on. The slight variations observed may readily be accounted for as due to slight temperature variations to which the E.M.F. of the Clark cell is very sensative, besides no special precautions were taken to exclude the effect of light, so the test was a very severe one.

These results obtained by rotating the cathode systems of the cadmium and Clark cells seem to confirm in a most decisive manner the validity of the observations of the last two years on the Clark and cadmium cells. The assumption that the "drift" of the E.M.F.

of the cadmium cell is due to changes in the cathode system seems justified, but the possibility that some of the observed decrease in E.M.F. might be at the amalgam of the anode, has not been overlooked. This was tested as follows: some of the old cadmium cells which are now distinctly lower than when they were first observed, were opened and the side tube (*B*) of the anode leg (*A*) of Fig. 1 was brought into contact with the liquid of the cell and the E.M.F. of the cathode leg measured with the new anode as well as with the old. Any difference in the E.M.F. would be due to differences between the old and the new anode.

Cell.	With the Old Anode.	With the New Anode.
*F*1	1.01832	1.01829
*F*2	1.01830	1.01830
*F*4	1.01833	1.01830
*C*2	1.01832	1.01827
*N*9	1.01616	1.01617

Cell *C*2 was made on November 21, 1903, with commercial mercurous sulphate, and was originally 1.01866. Cell *N*9 was one of the cells made in November, 1904, with only a little paste and is still decreasing. With the new anode the cells are about .00003 V. *lower*, so the change at the cathode has been even greater than indicated by the direct comparisons of the cells.

The foregoing experiments justify the conclusion that the cathode system of the cadmium cell, as at present constructed, is not a system in equilibrium and that the E.M.F. of the cell decreases with time. The rate of this "drift" depends on a number of factors, but if the paste in the cathode leg is about 2 cm. deep, the change is very slow. The cadmium cell, when properly constructed with electrolytic mercurous sulphate, which has been prepared and washed as previously described, has a value of 1.01843 V. at 25° C. and seems to be reproducible to about 2 parts in 100,000. Cells should be made from time to time to detect the presence and magnitude of the drift. For all ordinary purposes this cell is entirely satisfactory but, if there are no serious errors in the experiments recorded in this article, the cadmium cell as at present constructed can hardly supplant the Clark cell as a primary standard of E.M.F.

The Clark cell made with recrystallized zinc sulphate and elec-

trolytic mercurous sulphate which has been prepared and washed as described in this journal[1] has the value 1.43300 V. at 15° C. as determined by Dr. K. E. Guthe.[2] This value is also the average of all the best previous determinations of the value of the Clark cell in absolute units. The experiments described in this article have severely tested the Clark cell and with most favorable results. Several improvements and simplifications of this cell have been suggested by the work done are now being tested.

PRINCETON UNIVERSITY,
June, 1906.

[1] PHYS. REV., 22, 334, 1906.
[2] PHYS. REV., 22, 117, 1906.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-THIRD MEETING.

A JOINT meeting of the Physical Society with Section B of the American Association for the Advancement of Science was held in the Physical Laboratory of Cornell University, Ithaca, N. Y., June 29 to July 3, 1906.

Vice-president Sabine, of Section B, presided.

The following papers were presented:

1. A Young's Modulus Apparatus. B. B. BRACKETT.

2. Lecture Room Resistance Apparatus. B. B. BRACKETT.

3. Two Neglected Factors in the Determination of Musical Quality. WALLACE C. SABINE.

4. Silver Perchlorate as the Electrolyte for the Silver Coulometer. HENRY S. CARHART, H. H. WILLARD and W. D. HENDERSON.

5. A Lecture Experiment in Electrolytic Thermo-Electromotive Force. HENRY S. CARHART.

6. Note on the Graphical Representation of Non-Sinusoidal Alternating Currents. FREDERICK BEDELL.

7. The Dispersion of Silver Chloride. E. F. NICHOLS and W. S. DAY.

8. Properties of Electric Charges on Moving Conductors. E. F. NICHOLS.

9. The Separation of Electric Charges in a Metal by Centrifugal Acceleration. E. F. NICHOLS.

10. Comparative Observations on the Evolution of Gas from the Cathode with the Glow Current in Helium and Argon. CLARENCE A. SKINNER.

11. The Effect of Absorbed Hydrogen on the Photo-Electric Current. W. P. HOLMAN.

12. The Production of Ozone by the Becquerel Rays. HARRY S. HOWER.

13. The Production of Ozone by the Photo-Electric Current in Oxygen. HARRY S. HOWER.

14. Fluorescence Absorption in Resorufin. FRANCES WICKE.

15. Further Experiments on the Phosphorescence of Sidot Blende. E. L. NICHOLS and ERNEST MERRITT.

16. Magnetograph Records of Earthquakes with special reference to the San Francisco Earthquake of April 18, 1906. L. A. BAUER.

17. Rotation and Elliptic Polarization Produced by Iron Films in a Magnetic Field. W. D. HARRIS. Presented by CLARENCE A. SKINNER.

18. Coefficients of Linear Expansion at Low Temperatures. H. G. DORSEY.

19. New Diffraction Spirals. A. G. WEBSTER.

20. The Calibration of Capillary Tubes. WILLARD J. FISHER.

21. The Latent Heat of Recalescence in Iron and Steel. FRANK K. BAILEY.

22. Thermal and Electrical Effects in Soft Iron between 100° and 218° C. EDWIN H. HALL.

23. Note on Certain Aspects of Drude's Electronic Theory of Metallic Conduction. EDWIN H. HALL.

24. The Capacity and Resistance of Aluminum Anode Films. C. McC. GORDON.

25. Spark Potentials in Liquid Dielectrics. ROBERT F. EARHART.

26. Spark Potentials between a Point and a Plane for Small Distances. ROBERT E. EARHART.

27. Electric Double Refraction in CS_2 at High Temperatures. L. S. MORSE.

28. Electric Double Refraction in CS_2 at Low Potentials. L. S. MORSE.

29. A New Alternating Current Galvanometer. L. A. FREUDENBERGER.

30. The Temperature of the Moon. WM. W. COBLENTZ.

31. Infra-Red Reflection Spectra. WM. W. COBLENTZ.

It was decided to hold the fall meeting of the Society in Chicago.

Adjourned.

ERNEST MERRITT,
Secretary.

TALBOT'S LAW AS APPLIED TO THE ROTATING SECTORED DISK.[1]

BY E. P. HYDE.

IT is evident that in photometric measurements some method other than varying the distance would be of value in comparing the illumination due to light sources of different intensities. The rotating sectored disk offers such a method, but at once brings up the question of the accuracy of Talbot's law.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society on April 20, 1906.

It was therefore decided to investigate this law in its photometric application, namely, to determine whether the photometric effect of the light transmitted through a rotating sectored disk is proportional to the total angular opening of the disk. Previous work has been done on this subject by Plateau, Helmholtz, Fick, and others, and more recently by Ferry and Lummer and Brodhun.

Ferry verified the law for white light, but found errors of considerable magnitude when the lights compared were different in color. A thorough study of his work led to the conclusion that a number of experimental errors had been introduced. A more satisfactory investigation was made by Lummer and Brodhun who found the law verified but did not carry their research as far as seemed desirable.

A choice of the Nernst glower as a light source, led to a preliminary theoretical investigation to determine errors in its use, due to the assumption of the inverse square law. In connection with this a study was made of the radiation from a cylindrical source.

In the experimental work, a photometric bench of the ordinary Reichsanstalt form was used, with a Lummer-Brodhun photometer head. The electrical measurements were made on a potentiometer.

The glower of direct current type was mounted without globe or ballast, so that it could be rotated in a horizontal plane, the latter containing the photometric axis. In the measurements the glower was turned first with one side toward the photometer, then through 180 degrees, the mean of the two sets of readings being taken. To avoid air currents it was covered with a tall cylindrical hood carefully blackened and fitted with black velvet to prevent reflection. Another glower similarly mounted was used for a comparison lamp, being rigidly connected to the photometer head by two adjustable rods.

The substitution method was used, readings being taken with the disk in and out, the distance from the test glower to the photometer head being altered in the proper proportion.

The disks employed were accurately measured and were mounted on and driven by a small electric motor. The range of total openings was from 288 degrees to 10 degrees. To study the effect of color, red, green and blue glasses were inserted in succession in the eye piece of the photometer. Readings were also made with the Nernst used as a comparison lamp replaced by an incandescent lamp at low voltage.

Elaborate precautions were taken to eliminate all possible sources of error such as those due to distance, inequality of the ways, reflections, intensity of illumination, speed of the disks, the personal equation, etc.

The results obtained were plotted in the form of a curve, having angular openings as abscissæ and percentage deviations from the law of Talbot as ordinates. It was shown that for all angular openings the law

is verified for white light to within 0.3 per cent., which probably represents the limit of accuracy of the observations. It is verified also for colored light, and for difference in color between the sources, but not to such a high degree of accuracy.

Note on the Compound Interferometer.[1]

By C. W. Chamberlain.

In an article on "Short Spark Discharges" in *Phil. Mag.* (6), Vol. 9, p. 696 (1905), Professor C. Kinsley presents the following equations showing the relation between the actual movement of the carriage and the increase in the length of the path of the ray.

Let a = angle of incidence.

x = angle between mirrors A and B.

D_n = actual distance passed over by the ray between the mirrors due to a movement of the mirror B.

n = the number of the order, *i. e.*, n, gives the number of times the ray is reflected by the mirror B.

d = actual movement of the mirror B along the original path of the ray.

f_n = number of fringes that passed the cross hair of the microscope when the nth order of reflections was used.

λ = wave-length of the light employed.

$a = d \cos a$.

$$D_5 = \frac{4a}{\cos a} + \frac{4a}{\cos (a - 2x)} + \frac{2a}{\cos (a - 4x)}.$$

$$D_{10} = 4a\left\{\frac{1}{\cos a} + \frac{1}{\cos (a - 2x)} + \frac{1}{\cos (a - 4x)} + \frac{1}{\cos (a - 6x)} + \frac{1}{\cos (a - 8x)}\right\}.$$

$a = 22\frac{1}{2}°$. For the tenth order $x = 2\frac{1}{2}°$.

Substituting in the above equations,

$$d = \frac{D_{10}}{19.09}.$$

[1] Abstract of a paper presented at the Washington meeting of the Physical Society on April 21, 1906.

The above equations are based upon a misconception. The general equation is as follows:

$$D_n = 2d \cos nx \cos (n-1)x \left(\frac{1}{\cos nx \cos (n-1)x} + \frac{1}{\cos (n-1)x \cos (n-2)x} + \frac{1}{\cos (n-2)x \cos (n-3)x} + \cdots \frac{1}{\cos x} \right).$$

It thus appears that the sparking distances as measured by Professor Kinsley are 6.6 per cent. too small where he employed fringes of the tenth order, and 7.7 per cent. too small where he employed fringes of the fifth order.

COMPARATIVE OBSERVATIONS ON THE EVOLUTION OF GAS FROM THE CATHODE IN HELIUM AND ARGON.[1]

BY CLARENCE A. SKINNER.

AS aluminium and magnesium have been found to give off as cathodes hydrogen much more freely than the denser metals these were chosen for making the comparative observations in helium and argon.

Under an uninterrupted series of experiments six different cathodes of aluminium (circular disks, diam. 15 mm.) were tested — three in helium, and three in argon — with electric currents of one, two, and three milliamperes respectively in each gas. Observations were made on the change of gas pressure with duration of current. Notwithstanding the fact that the cathode fall in helium under the existing conditions was, for the same current, at least twice that in argon and hence the heating effect at the cathode twice as great, the rate of evolution of gas was practically the same in the two gases. With a current of one milliampere the evolution in the two gases was practically identical for the first nine minutes and also for the same period there was perfect agreement in rate with Faraday's law. At the end of fifteen minutes the results from argon were less than ten per cent. below the required value, while those from helium were somewhat lower still. With a current of two milliamperes, the evolution in helium was, during the first minute in excess, that in argon in agreement with the law. After that time and up to the end of six minutes the results in both followed the required rate, falling short gradually

[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906. To be published in full in Phil. Mag.

thereafter. With three milliamperes the results in both gases were excessive for the first minute, agreed with the law during the next two, then fell short rapidly thereafter. In each case about .05 c.c. of gas (atmospheric pressure) was given off from each square centimeter of aluminium before the rate of evolution fell below Faraday's law.

Similar results were obtained with magnesium cathodes.

These experiments support the assumption made earlier that the rate of evolution of gas from a given cathode is the same in different gases, and therefore tend to establish the fact that certain gases are absorbed by the anode likewise at a rate determined by Faraday's law.

Perchlorate of Silver as the Electrolyte in a Silver Coulometer.[1]

By Henry S. Carhart, H. H. Willard and W. D. Henderson.

THE object of this research is to find an electrolyte if possible that will be free from the difficulties presented by silver nitrate. These are, the looseness of the deposited crystals, leading to loss in washing, and the formation of a heavy anodic liquid, which must be kept away from the cathode as completely as possible. The research is made more important just at present by the reaffirmation of the definition of the international ampere in terms of the deposit of silver by electrolysis.

One of us (Mr. Willard) has devised a method of preparing the perchlorate of silver ($AgClO_4$) in a pure state, and we have made a fairly large number of trials to determine its behavior in comparison with silver nitrate in electrolysis. The results are encouraging, but a large amount of patient work must be done before any decided conclusions can be reached.

The starting point in the preparation of perchlorates is sodium perchlorate, which is now obtainable commercially. It may be readily made in large quantities in the laboratory by the electrolysis of sodium chlorate.

A saturated solution of the perchlorate is diluted with two and a half times its volume of hydrochloric acid and is then saturated with the gas. Most of the sodium is precipitated as chloride. The solution of hydrochloric and perchloric acids is evaporated until heavy white fumes appear. The residue then contains about sixty per cent. perchloric acid and a little sodium perchlorate. This crude product is then distilled, preferably in a vacuum. It can be distilled under atmospheric pressure, but it then

[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

suffers a little decomposition, with the production of chlorine and its oxides. These dissolve in the distillate and they may be removed by aspirating air through the warm solution.

To prepare silver perchlorate a suitable quantity of silver nitrate is weighed out and an amount of perchloric acid slightly in excess of the theoretical requirement is added. The temperature is gradually raised until the nitrate has dissolved and nitric acid is freely evolved. Finally the mass is maintained at 250° C. for several hours to remove the last traces of perchloric acid. A little chloride is formed at this temperature; but if the salt is heated in a vacuum, a much lower temperature will suffice to remove the acid and no chloride will be formed. It is necessary to have a neutral product, and for reasons that will appear later, it is impracticable to neutralize by adding silver oxide or carbonate. To make a solution, the silver perchlorate is dissolved in redistilled water and any chloride present is filtered out.

Up to the present our effort has been to compare the results obtained with silver perchlorate as compared with silver nitrate. The two coulometers were of the same pattern as those employed by Professor Guthe at the Bureau of Standards, and the porous cups were made at the same factory and from the same mould. The platinum vessels were ten centimeters in diameter and five cm. deep. When the anode was surrounded with filter paper, the cathode vessels used were eight cm. in diameter. Ten per cent. solutions of both salts were used. The treatment of the deposits has been the usual soaking, heating, and cooling in desiccators. In all the later comparisons the weighings have been made by means of a large and very excellent Rueprecht balance, and the differences have been obtained by balancing one cathode cup against the other.

The results thus far should be stated with reserve because the percentage differences between the nitrate and the perchlorate are very small, and the conclusions derived from one series of determinations are not always sustained by the next one. When the perchlorate of silver is neutralized with pure silver oxide, or is prepared by treating carbonate of silver with perchloride acid, the deposit from the perchlorate is invariably distinctly heavier than that from the nitrate prepared in the usual way. In this respect the perchlorate agrees with the nitrate, since both give a heavier deposit with a solution neutralized with the oxide or the carbonate.

The deposit from the perchlorate differs in appearance from that derived from the nitrate. Whether the anode is in a porous cup, or is enclosed in filter paper, the deposit is always lined or grooved in fine lines running from the bottom of the platinum cup to the top of the solution. The deposit from the nitrate is in more or less detached crystals, which do not adhere together so well as the grooved deposit when the electro-

lyte is the perchlorate. Hence the weighed washings from the nitrate are usually greater than from the perchlorate.

Two series of comparisons have recently been made, one with the anodes in porous cups, and the other with the anodes wrapped in Baker & Adamson's washed filter paper. In the first series the deposits from the perchlorate average 0.023 per cent. heavier than that from the nitrate. In one case only did the nitrate give a deposit heavier by an insignificant per cent.

In the other series with the filter paper, the deposit from the perchlorate average only 0.013 per cent. heavier, and in half of the series of six determinations the nitrate gave the heavier deposit. Taken all together, the comparisons thus far appear to show a slightly heavier deposit from the perchlorate, and at the same time the indications are that no reduction or other products are formed from the perchlorate and no complex anodic compound is present. We do not thus far find any advantage in using the porous cup; in fact the porous cup is objectionable from several points of view. Ordinary filter paper cannot be used, but the washed paper appears not to be objectionable. Further investigation will be necessary in order to settle this point definitely.

A Lecture Experiment in Electrolytic Thermo-Electromotive Force.[1]

By Henry S. Carhart.

IN the Helmholtz equation for the E.M.F. of a voltaic cell,

$$E = \frac{H}{Q} + T \cdot \frac{dE}{dT},$$

the second term is dependent on the temperature coefficient of the cell, and this coefficient is admittedly due to the thermo-electromotive forces at the several junctions of dissimilar substances in the cell. Whenever, therefore, the conditions are such that the heat of reaction is negligible, the first term, H/Q, becomes zero and only the second term remains. Such are approximately at least the conditions in a Helmholtz concentration cell. The E.M.F. of such a cell is thermoelectric in origin and should be represented by the second term of the Helmholtz equation.

A concentration cell with pure silver electrodes and solutions of silver nitrate, whose ratio of concentrations was 5.26, gave an E.M.F. at 30° of 0.0452 volt. The mean of two determinations of the temperature coefficient, dE/dT, was 0.000144. Whence E, calculated by the expression $T \cdot dE/dT$, is 0.000144×303 or 0.0436.

[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

A similar concentration cell with cadmium amalgam and one-tenth and one hundredth normal cadmium sulphate solutions had an E.M.F. at 22.35° C. of 0.034 volt. The mean temperature coefficient was 0.0001085. Whence the calculated value of E is 0.0001085×295.35 or 0.032. The calculated value in both cases is below the measured E.M.F., indicating that there is a little heat of reaction, due perhaps to mixing the solutions.

From the curve obtained by the author,[1] expressing the relation between the thermo-electromotive forces of $Zn - ZnSO_4$ and the corresponding concentrations of the zinc sulphate solution, the following equation may be derived:

$$dE = a \cdot T \cdot \frac{dC}{C}. \quad \text{Whence } E = a \cdot T \log C.$$

This expression is the potential difference at a single electrode. For two electrodes immersed in solutions of different concentrations, the expression becomes

$$E = a \cdot T \cdot \log \frac{C_2}{C_1}.$$

This equation will be recognized as the one derived by Nernst from the theory of osmotic pressure. The derivative of E with respect to T, is

$$\frac{dE}{dT} = a \cdot \log \frac{C}{C}.$$

Solve for the constant a, substitute in the above equation for E, and we get $E = T \cdot dE/dT$, the second term of the Helmholtz equation. We have thus the nexus between the Helmholtz and the Nernst equations, and at the same time it appears that the latter may be derived from thermo-electric data.

The lecture experiment of the paper is intended to illustrate electrolytic thermo-electromotive force. Two fine iron wires are soldered to the ends of a piece of "constantan" wire as a thermal couple. The junctions are placed in thin glass tubes and a little mercury is poured in to conduct heat. A helix of fine copper wire is wound closely around the end of each tube outside the junction of the iron and constantan. The tubes with their thermal junctions are then immersed in a concentrated solution of copper sulphate, and current is passed through by means of the copper wires. A sufficiently sensitive galvanometer shows that a difference of temperature is soon established between the copper electrodes, the anode, where the current encounters an opposing E.M.F., being the warmer. Heat is generated at the anode and absorbed at the cathode by the thermo-electromotive force.

[1] Transactions of the American Electrochemical Society, Vol. II., p. 123.